

LIGHT EMITTING POLYMERS

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The list of abbreviations

acac	acetylacetonate
bipy	2,2'-bipyridyl
BT	2,1,3-benzothiadiazole
BTPD-PFCB	triarylamine/perfluorocyclobutane containing polymer (Comp. 130)
BuLi	<i>n</i> -butyllithium
CDT	Cambridge Display Technology
CIE	chromaticity coordinates by the Comission Internationale de l'Éclairage, 1931
CN-PPV	poly(phenylene cyanovinylene)
cod	1,5-cyclooctadiene
DCM	dichloromethane
DMF	<i>N,N</i> -dimethylformamide
dppe	1,2-bis(diphenylphosphino)ethane
dppp	1,3-bis(diphenylphosphino)propane
DSC	differential scanning calorimetry
E_A	electron affinity, [eV]
EDTA	ethylenediaminetetraacetic acid
EH	2-ethylhexyl
EL	electroluminescence
Fl	fluorene
FWHM	full width at half maximum, [nm]
GPC	gel-permeating chromatography
HOMO	highest occupied molecular orbital
HTL	hole-transport layer
I_p	ionization potential, [eV]
ITO	indium tin oxide
LDA	lithium diisopropylamide
LEC	light-emitting electrochemical cell
LED	light emitting diode
LEP	light emitting polymer
LPPP	ladder poly(<i>p</i> -phenylene)
LUMO	lowest unoccupied molecular orbital
MEH-PPV	poly[2-methoxy-5-(2-ethylhexyloxy)- <i>p</i> -phenylene vinylene] [Comp. 13]
μ_+	hole mobility in a semiconductor, [cm ² /V s]
μ_-	electron mobility in a semiconductor, [cm ² /V s]
Ni(cod) ₂	bis(1,5-cyclooctadiene)nickel(0)
NIR	near infra-red
NTSC	National Television Standard Committee color specification
OLED	organic light emitting diode
OTV	oligo-2,5-thienylenevinylene
PANI	polyaniline
PAT	poly(3-alkylthiophene)
PBD	2-(4-biphenyl)-5-(4- <i>tert</i> -butylphenyl)-1,3,4-oxadiazole (Comp. 21)
PDHF	poly(9,9-dihexylfluorene) [Comp. 187]
PDI	polydispersity index
PEDOT	poly(3,4-ethylenedioxythiophene)
PF	polyfluorene

PFO	poly(9,9-dioctylfluorene) [Comp. 188]
PL	photoluminescence
PLED	polymeric light emitting diode
PMMA	poly(methyl methacrylate)
POSS	polyhedral oligomeric silsesquioxane
PPP	poly(<i>p</i> -phenylene)
PPV	poly(<i>p</i> -phenylene vinylene)
PT	polythiophene
PTV	poly-2,5-thienylenevinylene
PVK	poly(<i>N</i> -vinylcarbazole)
Q.E.	quantum efficiency
RGB	red-green-blue color specification
SEC	size exclusion chromatography
T_{dec}	decomposition temperature
T_{g}	glass transition temperature
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
THP	tetrahydro-2 <i>H</i> -pyran (protecting group)
TPD	tetraphenylbenzidine (Comp. 293)
TPP	tetraphenylporphyrine
UPS	ultraviolet photoelectron spectroscopy
$\Phi_{\text{EL}}^{\text{ex}}$	external quantum efficiency of electroluminescence
Φ_{PL}	quantum yield of photoluminescence
Zn*	Rieke zinc reagent
XPS	X-ray photoelectron spectroscopy

Introduction

The birth of the field of electroluminescent polymers is connected with the paper by Friend et al. in 1990¹ describing an electroluminescent (EL) device based on conjugated poly(p-phenylene vinylene) (PPV), although some polymer electroluminescence devices based on poly(*N*-vinyl)carbazole (PVK), doped with luminescent dyes have been reported by Partridge long before.^{2,3} In the former paper, a single layer of PPV, placed between ITO and Al electrodes, emitted green-yellow light under applied DC voltage. The device efficiency and relatively low turn-on voltage gave a promise for a possible technological progress to a stage of commercial application. It was clear that such progress would require not only improved device engineering technique, but also sophisticated control of the materials luminescence efficiency and electron/hole transporting properties, challenging the community of physical organic and polymer chemists.

From 1990s and till now, LEDs is probably the most important application maintaining the researchers' interest towards conjugated (conducting) polymers, although in recent years we witness a growing interest towards other relevant applications such as sensors and photovoltaics. Hundreds of academic research groups around the world have contributed to the development of electroluminescent polymers. An even more pronounced research activity is being held in industry. Several newly born R&D companies such as Cambridge Display Technologies (CDT, spin-off from Cambridge University), Covion Organic Semiconductors and UNIAX (spin-off from UCSB), are targeted at development of high efficiency, long life-time EL polymers. A huge commercial potential, connected with the possibility of solution fabrication of EL devices, and, particularly, flat and/or flexible displays, attracted in the business such industrial giants as Dow Chemical, DuPont, IBM, Kodak and Philips.⁴

Light-emitting polymers (LEPs) have been a subject of many review articles, which dealt with various aspects of the design, the synthesis and the applications of different classes of LEPs (Table 1). Very insightful reviews of a general character have been presented by Holmes et al. (1998, Table 1), Friend et al. (1999, Table 1), and Bäuerle et al. (2000, Table 1). Among the recent papers, one of the most complete accounts was written by Ackelrud (2003, Table 1). However, none of the mentioned papers is comprehensive in covering different classes of EL polymers, and cannot be taken as a single source of information on this matter.

Table 1. The most important reviews covering the synthesis and application of light-emitting polymers.

Year	Title	Authors	Publication
1993	Conjugated polymer light-emitting diodes	A. R. Brown, N. C. Greenham, R. W. Gymer, K. Pichler, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. Kraft, A. B. Holmes	in: <i>Intrinsically Conducting Polymers: An Emerging Technology</i> , NATO ASI Series, Series E: Applied Sciences 246: 87–106
1993	Conjugated Polymer Electroluminescence	D. D. C. Bradley	<i>Synth. Metals</i> 54: 401–415
1994	Light-emitting diodes fabricated with conjugated polymers - recent progress	D. R. Baigent, N. C. Greenham, J. Gruener, R. N. Marks, R. H. Friend, S. C. Moratti, A. B. Holmes	<i>Synth. Met.</i> 67: 3–10
1996	Conjugated Polymer Electroluminescence	R. H. Friend, N. C. Greenham	in: <i>Physical Properties of Polymers Handbook</i> (J.E. Mark ed.) AIP Press, NY 1996, 479–487.
1997	Polymer Electroluminescent Devices	Y. Yang	<i>MRS Bulletin</i> : June 1997, 31–38

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|------|---|---|--|
| 1997 | Light-emitting Polymers: Increasing promise | W. C. Holton | <i>Solid State Technology</i> 40: 163–169 |
| 1998 | Electroluminescent Conjugated Polymers—Seeing Polymers in a New Light | A. Kraft, A. C. Grimsdale, A. W. Holmes* | <i>Angew. Chem. Int. Ed.</i> 37: 402–428 |
| 1998 | The Chemistry of Electroluminescent Organic Materials | J. L. Segura | <i>Acta Polym.</i> 49: 319–344 |
| 1998 | Design and Synthesis of Polymers for Light-emitting Diodes | A. Greiner | <i>Polym. Adv. Technol.</i> 9: 371–389 |
| 1998 | Optical Applications | M. G. Harrison, R. H. Friend | in: <i>Electronic Materials: The Oligomer Approach</i> (K. Müllen, G. Wegner eds.), Wiley-VCH, Weinheim 1998, 515–558. |
| 1998 | The Chemistry and Uses of Polyphenylenevinylenes | S. C. Moratti | in: <i>Handbook of Conducting Polymers</i> (T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds eds.), Marcel Dekker, NY-Basel-Hong Kong 1998, 343–361 |
| 1998 | Conjugated Ladder-Type Structures | U. Scherf | in: <i>Handbook of Conducting Polymers</i> (T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds eds.), Marcel Dekker, NY-Basel-Hong Kong 1998, 363–379 |
| 1998 | Electroluminescence in Conjugated Polymers | R. H. Friend, N. C. Greenham | in: <i>Handbook of Conducting Polymers</i> (T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds eds.), Marcel Dekker, NY-Basel-Hong Kong 1998, 823–845 |
| 1998 | Fundamentals of Electroluminescence in Paraphenylene-Type Conjugated Polymers and Oligomers | G. Leising, S. Tasch, W. Graupner | in: <i>Handbook of Conducting Polymers</i> (T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds eds.), Marcel Dekker, NY-Basel-Hong Kong 1998, 847–880 |
| 1999 | Electro-optical Polythiophene Devices | M. Granström, M. G. Harrison, R. H. Friend | in: <i>Handbook of Oligo- and Polythiophenes</i> (D. Fichou ed.), Wiley-VCH, Weinheim 1999, 405–458. |
| 1999 | Electroluminescence in Conjugated Polymers | R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlung, W. R. Salaneck | <i>Nature</i> 397: 121–127 |
| 1999 | Polarized Luminescence from Oriented | M. Grell, D. D. C. Bradley | <i>Adv. Mater.</i> 11: 895– |

	Molecular Materials		905
1999	Ladder-Type Materials	U. Scherf	<i>J. Mater. Chem.</i> 9: 1853–1864
1999	Electroluminescence in Organics	J. Kalinowski	<i>J. Phys D: Appl. Phys.</i> 32: R179–R250
2000	The Electroluminescence of Organic Materials	U. Mitschke, P. Bäuerle*	<i>J. Mater. Chem.</i> 10: 1471–1507
2000	Progress in Light-Emitting Polymers	M. T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu	<i>Adv. Mater.</i> 12: 1737–1750
2000	Synthesis of Conjugated Polymers for Application in Light-Emitting Diodes (PLEDs)	R. E. Martin, F. Geneste, A. B. Holmes	<i>C. R. Acad. Sci. Paris</i> , t. 1, Série IV: 447–470
2000	Blue Light Emitting Polymers	D. Y. Kim, H. N. Cho, C. Y. Kim*	<i>Prog. Polym. Sci.</i> 25: 1089–1139
2000	Fluorene-Based Polymers – Preparation and Applications	M. Bernius, M. Inbasekaran, E. Woo, W. Wu, L. Wujk`owski	<i>J. Mater. Sci.: Mater. Electronics</i> 11: 111–116
2000	Poly(aryleneethynylene)s: Syntheses, Properties, Structures, and Applications	U. H. F. Bunz	<i>Chem. Rev.</i> 100: 1605–1644
2000	Semiconducting (Conjugated) Polymers as Materials for Solid-State Lasers	M. D. McGehee, A. J. Heeger	<i>Adv. Mater</i> 12: 1655–1668
2001	Conjugated Polymers for Light-Emitting Applications	L. Dai, B. Winkler, L. Dong, L. Tong, A. W. H. Mau	<i>Adv. Mater.</i> 13: 915–925
2001	Polyfluorenes: Twenty Years of Progress	M. Leclerc	<i>J. Polym. Sci. Part A: Polym. Chem.</i> 39: 2867–2873
2001	Polyfluorene Homopolymers: Conjugated Liquid-Crystalline Polymers for Bright Emission and Polarized Electroluminescence	D. Neher	<i>Macrom. Rapid Commun.</i> 22: 1365–1385.
2002	Recent Developments in Light-Emitting Polymers	I. D. Rees, K. L. Robinson, A. B. Holmes, C. R. Towns, R. O'Dell	<i>MRS Bulletin</i> , June 2002, 451–455
2002	Semiconducting Polyfluorenes – Towards Reliable Structure-Property Relationships	U. Scherf, E. J. W. List	<i>Adv. Mater.</i> 14: 477–487
2003	Conjugated Polymers as Molecular Materials: How Chain Conformation and Film Morphology Influence Energy Transfer and Interchain Interactions	B. J. Schwartz	<i>Annual Rev. Phys. Chem.</i> 54: 141–172
2003	Carbazole-Containing Polymers: Synthesis, Properties and Applications	J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski*	<i>Progr. Polym. Sci.</i> 29: 1297–1353
2003	Electroluminescent Polymers	L. Akcelrud	<i>Prog. Polym. Sci.</i> 28: 875–962
2004	Recent Development of Polyfluorene-Based RGB Materials for Light Emitting Diodes	W. Wu, M. Inbasekaran, M. Hudack, D. Welsh, W. Yu, Y. Cheng, C. Wang, S. Kram, M. Tacey, M. Bernius, R. Fletcher, K. Kiszka, S. Munger, J. O'Brien	<i>Microelectronics Journal</i> 35: 343–348
2004	Synthesis of Conjugated Oligomers and Polymers: the Organometallic Way	F. Babudri, G. M. Farinola, F. Naso	<i>J. Mater. Chem.</i> 14: 11–34

The current chapter was written with an ambition to be the most complete collection of the references to existing EL polymers, while discussing the problems of their design, synthesis, physical properties and the resulting LED performance. In what follows we describe main classes of light-emitting polymers, which have been studied since ca. 1990 through mid-2004. Although it would not be possible to cover all related literature in a single chapter (or even a separate book), an attempt has been made to cover all important polymeric electroluminescent materials, which have been communicated in scientific journals (and, when relevant, in the patents). However, considering enormous amount of publications appearing in a broad variety of journals each year, it is not

impossible that some important paper describing a new LEP did not come to our attention. The chapter is written from the viewpoint of organic materials chemist. It includes description of basic synthetic methods, and, through a diversity of discussed structural variations influencing optoelectronic and electroluminescent properties, uncover some general structure-properties relationships in the described materials. A short description of LED structure is given along with the data on EL performance, whenever possible. However, a chemist reader should be warned of limitations of comparison of the EL data obtained by different groups (even for the same device structure). The conclusions on the practical value of different materials, beyond those given in the chapter, should be made with great care. In the Outlook section, we will list some of the best-performing LEP, and give our understanding of where the field is going. Finally, in the Appendix the interested reader can find some practical synthetic methods for different classes of LEPs.

1. Poly(phenylene vinylenes) (PPVs)

Poly(*p*-phenylene vinylene) (PPV, **Comp. 1**) is a highly stable conjugated polymer. Its yellow color is due to an absorption band centered at ~400–420 nm (depending on the method of synthesis) with an on-set corresponding to a band gap of ~2.5 eV.⁵ The HOMO and LUMO levels in PPV can be accessed in cyclic voltammetry experiments, which, under proper conditions, reveal chemically reversible oxidation and reductions waves (Figure 1). The deduced electrochemical gap corresponds reasonably well to the optical band gap. Being a relatively good electron donor, PPV and its derivatives can be chemically doped by strong oxidizing agents and strong acids, affording highly conductive *p*-doped materials (with conductivity up to ~10⁴ S/cm⁵). The yellow-green fluorescence of PPV **Comp. 1** is featured by a vibronically structured emission band with peaks maxima at 520 and 551 nm (Figure 1).

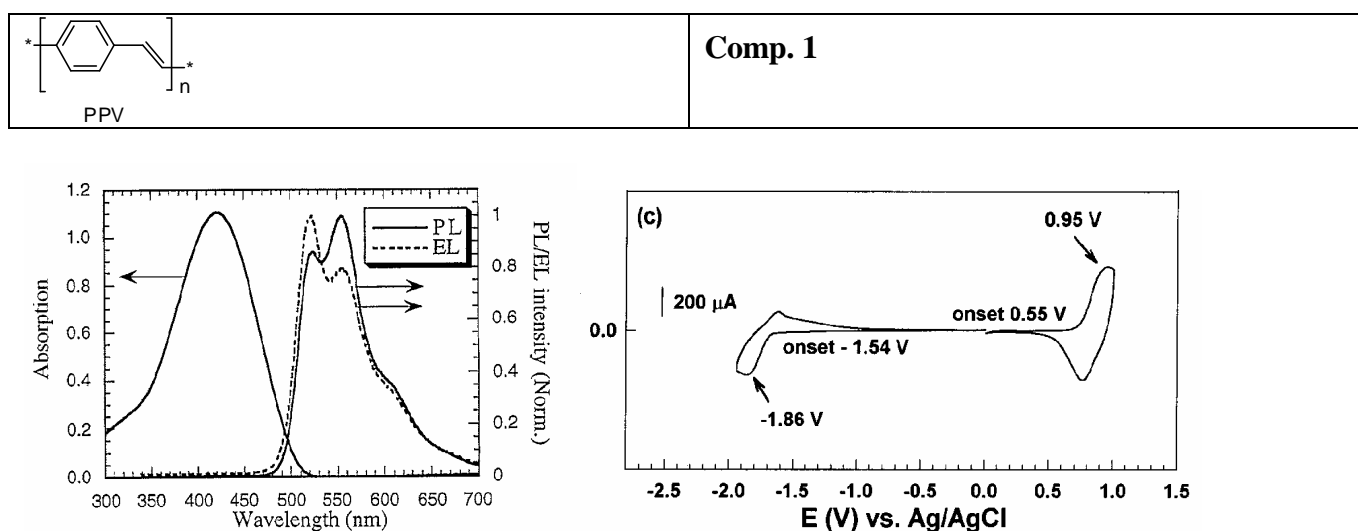


Figure 1. Left: typical absorption, photo- and electroluminescence spectra of PPV (given for dialkyl-PPV **Comp. 28**; from ref. 88, © Elsevier Science); Right: cyclic voltammetry of dialkoxy-PPV (**Comp. 13**). [From Ref. 172, © American Chemical Society].

The discovery of the electroluminescence in PPV in 1990 gave birth to a tremendous growth of interest to polymer LEDs (PLEDs).¹ Since then, numerous derivatives and analogues of PPV with tailored light-emitting properties have been synthesized, and a number of reviews and accounts described the synthesis and the EL properties of these materials.^{6,7,8,9,10,11,12,13,14,15,16} Many new applications of PPV polymers, as solid state lasing,^{17,18} photovoltaics,¹⁹ etc. have been explored, although they are beyond the scopes of this book. Below we give a general overview of basic methods of synthesis of PPV derivatives and the design of PPV materials with controllable properties, as it was widely explored for the last 15 years in order to create high performance PLEDs.

1.1. Synthetic routes to PPV.

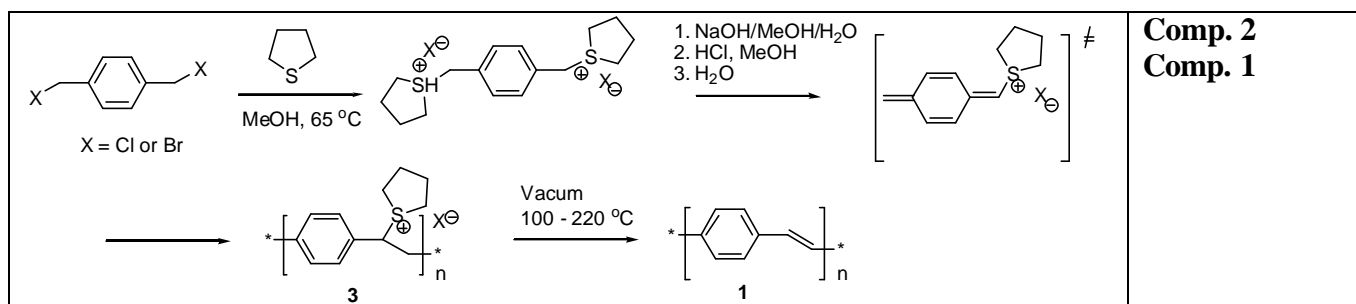
There are number of synthetic strategies elaborated for preparation of PPV homo- and co-polymers:²⁰

1. Thermoconversion (Wessling-Zimmerman route)
2. Chemical vapor deposition (CVD)
3. Ring-opening metathesis polymerization (ROMP)

4. The Gilch polycondensation
5. Chlorine precursor route (ROMP) (Gilch modification)
6. Non-ionic route (Gilch modification)
7. Knoevenagel polycondensation
8. Heck coupling polymerization
9. Wittig(-Horner) Condensation
10. Miscellaneous.

1.1.1 Thermoconversion route

Since PPV itself is insoluble and difficult to process, the most widely used method, developed in the early 60's by Wessling and Zimmerman, is thermoconversion of a processable sulfonium intermediate **Comp. 2** (Scheme 1).²¹ The polymer **Comp. 2** is soluble in methanol and can be spin-coated to give a high quality thin film, heating of which results in formation of PPV **Comp. 1** via elimination of hydrogen halide and tetrahydrothiophene. Under proper conditions, the thermoconversion can give pin-hole free thin films of PPV suitable for PLED fabrication. The conversion temperature can be reduced to 100 °C by using bromide derivatives instead of chlorides, thus enabling fabrication of PLED on flexible substrates.²²



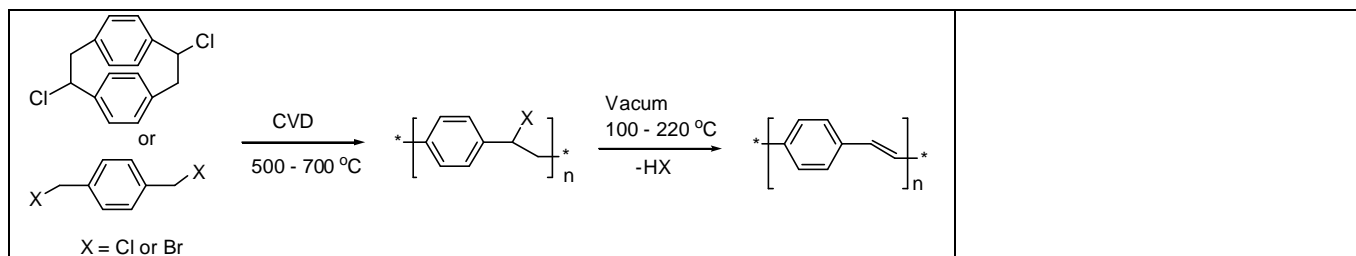
Scheme 1. The Wessling-Zimmerman precursor route to PPV.

The issues of low stability of the precursor polymer **Comp. 2** and extremely unpleasant odor of the mercaptane by-product can be resolved by substitution of the sulfonium leaving groups with a methoxy group (under acidic catalysis). The methoxy-substituted precursor polymer requires very harsh conditions for conversion in PPV (HCl gas at 220 °C).²³ On the other hand, the resulting PPV material showed significantly improved photophysical properties (more resolved vibronic structure of the absorbance, higher third-order non-linearity) which was explained by higher degree of order of the polymer chains.²⁴ Some other method modifications, as employment of a xanthate leaving group,^{25,26} or replacing the chloride ion (in precursor **Comp. 2**) with dodecylbenzenesulfonate ion²⁷ were reported. For the later, the long chain counter-ion facilitates processing of the precursor polymer in Langmuir-Blodgett films.

1.1.2 Chemical vapor deposition (CVD)

Another synthetic method, applicable for processing PPV in thin films is chemical vapor deposition (CVD) of dichloro-para[2.2]cyclophane²⁸ or dichloro-*p*-xylene²⁹ (Scheme 2). This method, though it can afford uniform and patterned thin films,³⁰ requires heating at 500–700 °C, which may give rise to by-product impurities. So harsh conditions and difficulties of complete removal of the

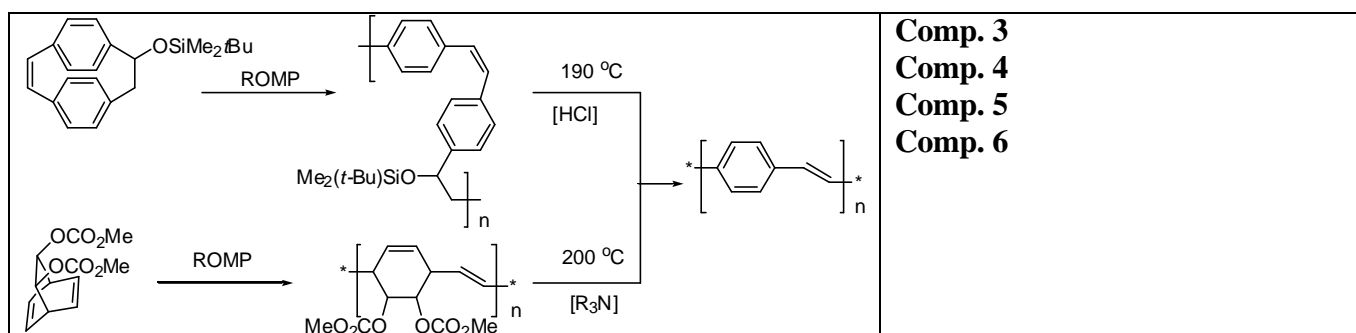
halogen (second stage) result in ill-defined material, which afford very low performance PLEDs (maximal brightness of 20 cd/m²).^{30b}



Scheme 2. Chemical vapor deposition route to PPV.

1.1.3 Ring opening metathesis polymerization (ROMP)

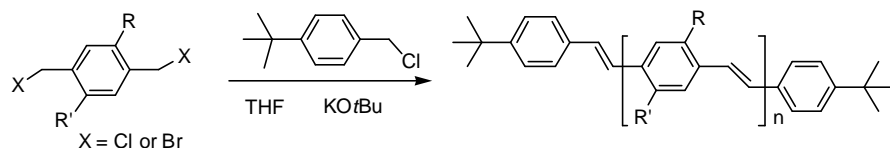
This drawback of CVD method is eliminated in ring-opening metathesis polymerization (ROMP), which is based on a catalytic (e.g., molybdenum carbene catalyst) reaction, occurring in rather mild conditions (Scheme 3). A living ROMP reaction of paracyclophane **Comp. 3** or bicyclooctadiene **Comp. 5** results in soluble precursors of PPV, polymers **Comp. 4**³¹ and **Comp. 6**³², respectively, with rather low polydispersity. In spite of all cis- (for **Comp. 4**) and cis/trans- (for **Comp. 6**) configuration, these polymers can be converted into all-trans PPV by moderate heating under acid/base catalysis. However, the film-forming properties of ROMP precursors are usually rather poor, resulting in poor uniformity of the PPV films.



Scheme 3. ROMP route to PPV.

1.1.4 Gilch PPV route

A general and most widely used synthesis of PPV derivatives was introduced by Gilch.³³ This method avoids high temperature conditions and occurs through base-promoted 1,6-elimination of 1,4-bis(chloro/bromo-methyl)benzenes **Comp. 7** (Scheme 4). For device applications, the as-synthesized PPV materials need to be soluble in organic solvents, otherwise the as-formed polymer powder is completely unprocessable. Alkyl-, alkyloxy- and other substituted monomers giving soluble PPVs have been employed in this reaction. The mechanism of the Gilch polymerization is still a subject of some controversy.^{34,35,36a} It is well accepted to proceed through a reactive quinodimethane intermediate, followed by either a radical or a living chain anionic polymerization. A molecular weight decrease upon addition of chain-transfer radical agent (TEMPO) was interpreted as a sign of the radical polymerization mechanism,³⁷ although the same effect imposed by nucleophilic initiator (4-*tert*-butylbenzylchloride) was taken as a confirmation of the nucleophilic chain growth mechanism.³⁵ In the



Scheme 5. End-capping modification of the Gilch polymerization.

1.1.5 Chlorine precursor route (CPR)

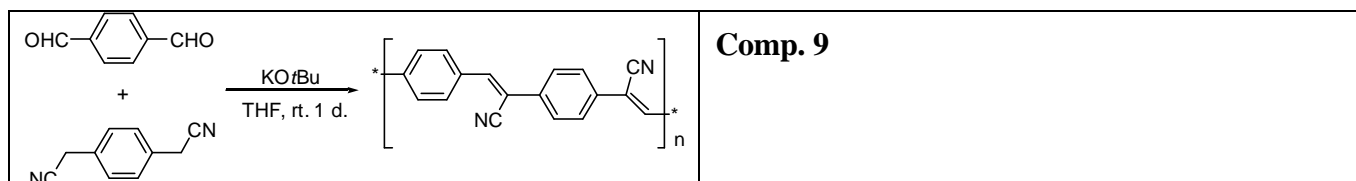
An important modification of Gilch polymerization (also known as chlorine precursor route, CPR), introduced by Swatos and Gordon in 1990, is based on using one equivalent of the base (instead of four in classical Gilch method) to stop the polymerization on the stage of formation of the precursor polymer **Comp. 8** (Scheme 4).^{39,41} Polymer **Comp. 8** is a very soluble material and can be spin-coated to afford high quality films. Thermal annealing at 230–280 °C results in elimination of hydrogen chloride and affords the PPV material in high yield.

1.1.6 Non-ionic route

Another extension of the Gilch polymerization approach, similar to the CPR method, was developed by Vanderzande et al.⁴² They have substituted one of chlorine atoms in the monomer **Comp. 7** with alkylsulfinyl group [BuS(O)], so as the resulting “precursor polymer” **Comp. 8** would not contain any chlorine. The alkylsulfinyl group can be removed in non-ionic process by simple heating the monomer at ~110 °C for few hours. The process can be attractive for applications, where the low halogen content is a critical issue, although the EL efficiency of PPV, prepared by this method is few times lower than that prepared by traditional Gilch polymerization (presumably, due to defects in the polymer structure).⁴²

1.1.7 Knoevenagel condensation

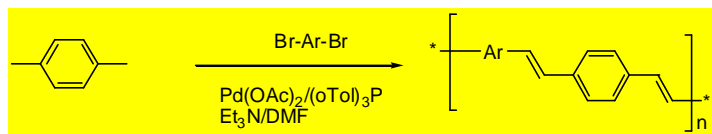
Knoevenagel condensation, based on the reaction of aldehyde group with active methylene component, was one of the first methods used for synthesis of PPV derivatives.⁴³ In general, it requires strong electron acceptor substituents (as CN) in the methylene component (Scheme 6). The method delivers PPV containing cyano substituents on the vinylene units (**Comp. 9**), and numerous substituted CN-PPV homo- and co-polymers have been synthesized.⁴⁴ Recently, ruthenium-based catalysis ($\text{RuH}_2(\text{PPh}_3)_4/\text{dppe}$) was used to replace strong base (as KOtBu) in Knoevenagel-type synthesis of CN-PPV, which brings the advantage of neutral and mild reaction conditions.⁴⁵



Scheme 6. Knoevenagel condensation route to PPV.

1.1.8 Heck coupling

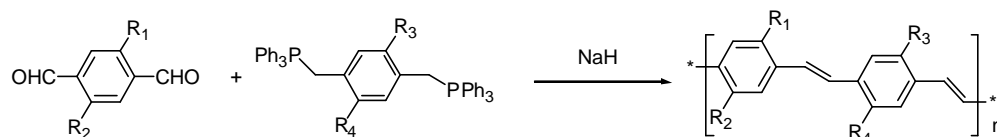
The PPV polymer chain can also be constructed by Heck coupling of aromatic dihalides with a divinylbenzene. In contrast to the above described methods, the Heck coupling is a Pd-catalyzed reaction occurring in very mild conditions. The polymerization normally leads to all-*trans* geometry with very few side reactions (Scheme 7).⁴⁶ Although this method is somewhat complicated as for the preparation of PPV homopolymers, the Heck-type synthesis of unsubstituted PPV and its methylated, trifluoromethylated and phenylated derivatives from divinylbenzene and dibromobenzene, dibromobenzene and ethylene, or bromovinylbenzene (self-coupling) was demonstrated.⁴⁷ Now, this method is of great utilization in preparation of alternating co-polymers (see section 1.3).



Scheme 7. Heck coupling route to synthesis of PPV co-polymers. *{The scheme is wrong! Why did you change it?}*

1.1.9 Wittig(-Horner) Condensation

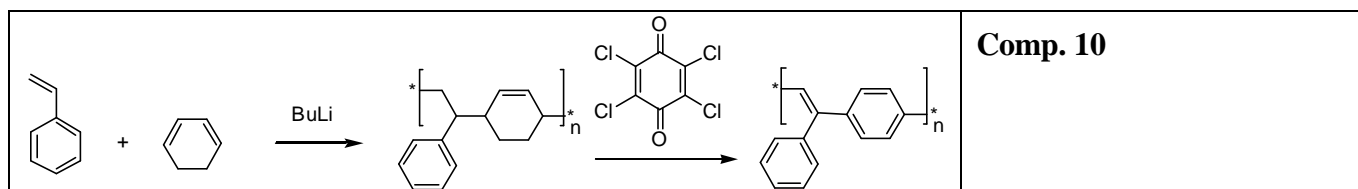
Wittig or Wittig-Horner condensation between substituted terephthalaldehydes and *p*-xylenediylphosphonium salts is also extensively used in preparation of alternating PPV co-polymers, e.g., containing different substituents in adjacent phenylene units (Scheme 8).⁴⁸



Scheme 8. Wittig condensation route to PPV.

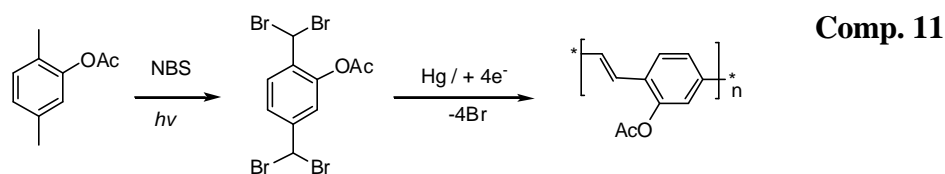
1.1.10 Miscellaneous.

A totally different route based on dehydrogenation of a saturated polymer precursor was introduced by Francois et al. (Scheme 9).⁴⁹ The method is based on anionic co-polymerization of cyclohexanediene with styrene, followed by oxidation with chloranil. Due to possible coupling of two styrene (or two cyclohexanediene) molecules, a block co-polymer, containing oligo(phenylene vinylene) units separated by oligo(phenylacetylene) and oligo(phenylene) blocks is obtained. To the best of our knowledge, it was, so far, used only in synthesis of phenyl-substituted PPV **Comp. 10**.



Scheme 9. Synthesis of phenyl-PPV by dehydrogenation route.

Akcelrud et al. reported preparation of acetoxy-PPV **Comp. 11** via controlled potential electrolysis of $\alpha,\alpha,\alpha',\alpha'$ -tetrabromoxylene precursor on a mercury electrode in $\text{Et}_4\text{NBr}/\text{DMF}$ electrolyte solution (Scheme 10).⁵⁰ However, the only structural characterization reported was UV-Vis and fluorescence spectra.

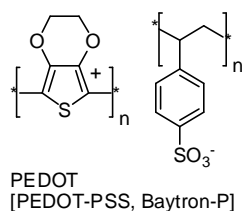


Scheme 10. Synthesis of acetoxy-PPV by electroreduction.

Below we describe the application of the described reactions to synthesis of PPV derivatives with tailored properties for PLEDs.

1.2. Substituted PPV homopolymers

The first conjugated polymer LED (PLED) was prepared by Friend et al. by sandwiching unsubstituted PPV **Comp. 1** (prepared by Wessling-Zimmerman reaction) between transparent ITO anode and Al cathode. It showed the maximal external Q.E. of only 0.01% at room temperature (0.05% at 120 K), and required 14 V to turn-on.¹ This low efficiency has several reasons, among which is disbalance of hole/electron injection barriers. The efficiency could be improved to 0.1% by using a lower work-function electrode (Ca).⁵¹ However, Ca is a highly reactive metal, which complicates the fabrication process and reduces the device stability. Alternatively, the EL can be improved by a factor of 30 by placing an electron transporting layer (oxadiazole based non-conjugated polymer) between PPV **Comp. 1** and Al electrode.⁵² On the way to electrically pumped lasers, Friend et al. reported exceptionally high peak brightness PLEDs based on PPV **Comp. 1**.⁵³ Applying a short pulsed voltage of ~10–40 V (pulse width 100–200 ns), the brightness of $5 \times 10^6 \text{ cd/m}^2$ has been achieved for a device ITO/PEDOT/**Comp. 1**/Al [PEDOT is poly(3,4-ethylenedioxythiophene)]. Although a relatively high EL efficiency (2.8 cd/A) was found in this device, the authors mention that it is still the device efficiency, and not the brightness, which limits the laser action.



As will be shown throughout the chapter, the parent PPV **Comp. 1** is extensively used as a hole transporting layer in combination with other electroluminescent polymers. Recently, improved photostability of organic-inorganic hybriide EL material prepared by incorporating PPV **Comp. 1** into zeolite capsules was described.⁵⁴ Although the material showed only weak EL (at driving voltage of 2.5 V), the authors are enthusiastic about the potential of this approach.

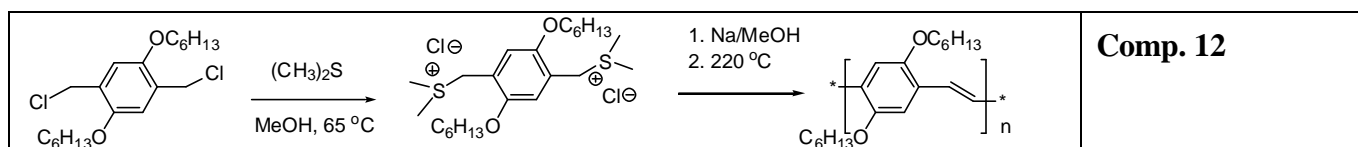
Modifications of the chemical structure of PPV provide various opportunities for tuning the optical properties of this material. The most explored modification was introducing the substituents in the benzene ring. These include alkyl, alkoxy and silyl-substituents substituents, aromatic functional

side groups and electron releasing/withdrawing groups, as discussed in details in the following sections.

One should, however, bear in mind that not only molecular structure of the polymers but also their supramolecular organization defines the performance of PLED. Thermal annealing of the films and other ordering techniques are widely used to change properties of the polymers. Particularly, solvents used for casting the film and the casting procedure can substantially change the supramolecular organization of the polymer and, thus, the performance of PLED. Single molecule fluorescence correlation spectroscopy studies confirms that the chain collapse and orientation of the single molecules of CN-PPV (**Comp. 9**) and MEH-PPV (**Comp. 13**) are highly influenced by the choice of the solvent: the production of oriented species is strongly favored in “poorer” solvents, where the polymer chains have more compact solution-phase structures.⁵⁵

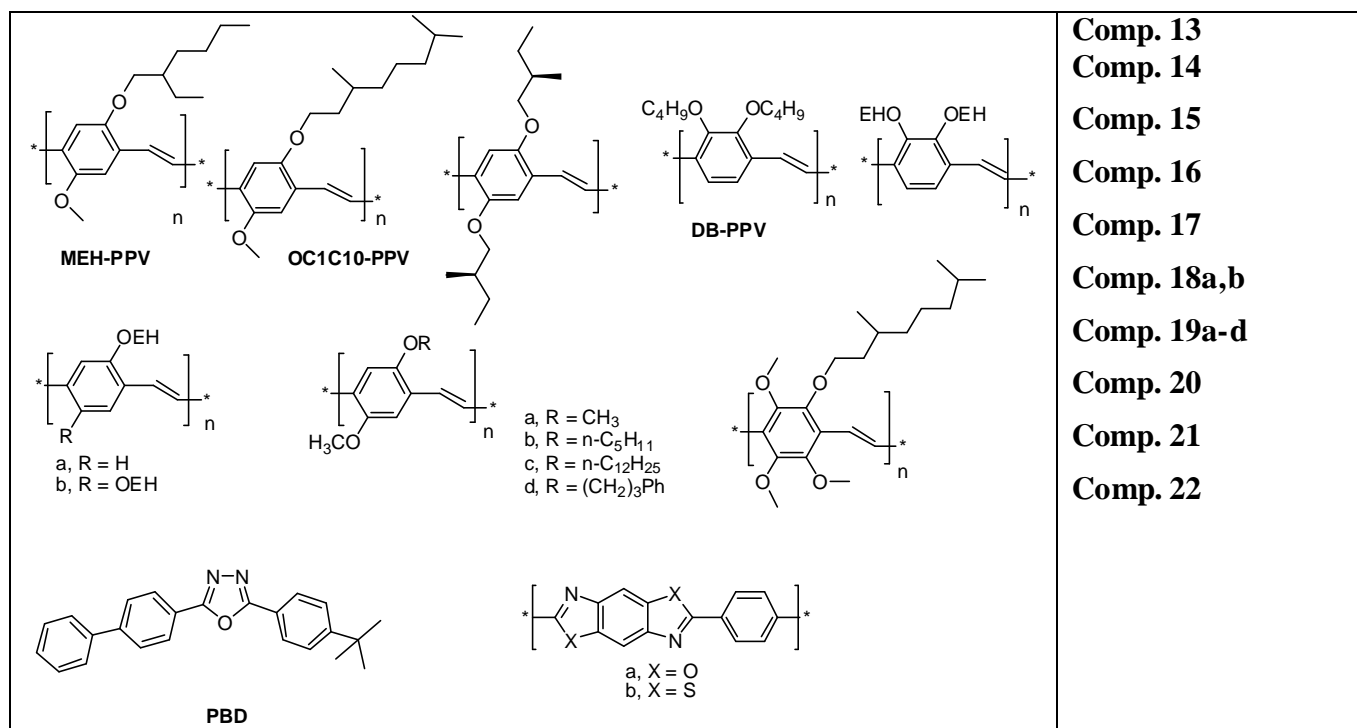
1.2.1 Alkoxy substituted PPVs

The insolubility of the PPV and, thus, the need for conversion of the precursor polymer on the last stage, under rather harsh conditions, is an obvious drawback for wide application of these materials. The obvious route to increase the solubility of the PPV would be introducing long-chain substituents. Although several groups synthesized and studied dimethoxy and diethoxy PPV derivatives starting from 1970, aiming at high stability conducting polymers,^{56,57} only dihexyloxy derivative, DH-PPV **Comp. 12**, prepared by Wudl et al. by thermal treatment of the sulfonium salt, appeared to be soluble in common organic solvents (Scheme 11).⁵⁸



Scheme 11. Synthesis of the first soluble PPV derivative, DH-PPV.⁵⁸

However, the solubility of this material at room temperature was still not high enough. The simple elongation of the substituents results in a “side-chain crystallization effect” and does not increase the solubility. To solve the problem, Wudl and Srdanov came up with a highly asymmetric substituents pattern (methoxy/2-ethylhexyloxy) for the synthesis of polymer **Comp. 13** (well-known as MEH-PPV) via Gilch polymerization route.⁵⁹ The side chain disorder brought by two different substituents as well as non-planar structure and optical isomers (due to stereogenic 2-ethylhexyloxy substituents) result in high solubility of this polymer in common organic solvents (toluene, chloroform, THF, etc.), in spite of extremely high molecular weight ($>10^6$ D). So high molecular weight can result in gelation of the polymer, and several attempts of controlling the polymerization degree via introducing end-capping reagents were undertaken.^{35,36} Also, studies by Burn et al. suggest that aggregation of MEH-PPV in solutions might affect the molecular weight determination, and lower M_n values have been obtained when analyzing highly diluted MEH-PPV solutions.⁶⁰ Completely insoluble form of MEH-PPV, which can be useful for preparation of multi-layer PLEDs was prepared by the same group via chlorine precursor route (using less than 1 equivalent of the base).⁶¹



MEH-PPV is a bright-orange material ($\lambda_{\max} \sim 490$ nm); upon photoexcitation it produces a red-orange emission ($\lambda_{\text{PL}} \sim 590$ nm). For the last decade, MEH-PPV has been one of the most studied electroluminescent materials.^{62,63,64,65,66,67,68,69,70,71,72,73} It was used as a standard LEP for demonstration of several innovative concepts in fabrication of PLEDs, including light-emitting electrochemical cells (LEC),⁶³ microstructuring the polymer layer for increased light out-put,⁶⁹ application of transparent polymer electrodes [doped polyaniline (PANI) or PEDOT films] in place of ITO,⁶⁵ nanocomposites with inorganic materials,^{67,69} etc. The first LEDs fabricated with this material were reported to show the external Q.E. of 0.05% in ITO/**Comp. 13**/In configuration and $\sim 1\%$ in ITO/**Comp. 13**/Ca configuration.⁶² External Q.E. of 1% can also be achieved with Al electrode in LEC device, using a blend of MEH-PPV, poly(ethyleneoxide) and electrolyte,⁶³ whereas the Q.E. less than 0.4% was achieved by the same group in same device using unsubstituted PPV **Comp. 1**.⁶⁴ Numerous improvements of the EL performance of MEH-PPV by blending this polymer with different organic and inorganic materials were reported. Highly efficient PLEDs (external Q.E. of 2%, maximal brightness of 10,000 cd/m²) were fabricated by adding SiO₂ nanoparticles to the MEH-PPV layer (between ITO and Ca electrodes).⁶⁷ The $\Phi_{\text{EL}}^{\text{ext}}$ of 1.3% was obtained by blending MEH-PPV with an electron transport material PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, (**Comp. 21**)].⁶⁸ More recently, the efficiency up to 2.5% was reported for multilayer PLEDs with additional polybenzobisazole (**Comp. 22**) electron-transporting layer (ETL) (ITO/PEDOT/**Comp. 13**/**Comp. 22b**/Al).⁷¹ Very high Q.E. values have been also obtained blending MEH-PPV with lithium organophosphonate surfactant (2.3%⁶⁵) or carbazole-thiophene co-polymers (3.8%⁷²). Recent results from Wong et al. show a two orders of magnitude increase of the EL efficiency (up to 2.7 cd/A, maximal brightness up to 5,500 cd/m²) of the ITO/MEH-PPV/Al device upon simple dilution of the MEH-PPV with poly(ethylene glycole) (PEG).⁷³

The 2-ethylhexyl substituent (EH) became a very popular side-chain group for synthesis of soluble conjugated polymers of different classes, but other branched alkyloxy substituents have been also introduced in the PPV backbone. For example, polymer **Comp. 14** substituted with a 3,7-dimethyloctyl-1 group showed a very similar electronic behavior to that of MEH-PPV, but an

additional branching further improved its solubility and the film-forming properties.^{42,74} The PLEDs with EL efficiency of 1.2 cd/A (with maximal brightness 4000 cd/m²)⁴² and even higher, 2.1 cd/A (2.5 lm/W)⁷⁴ and ~3 cd/A⁷⁵ have been reported fabricated with polymer **Comp. 14**. A systematic study of lifetime and degradation effects in PLEDs was reported for this polymer.⁷⁶ At low brightness level of ~100 cd/m² half-life times around 20,000 h was achieved. The device stability strongly depends on the operation temperature (Figure 2), and the authors suggested that electron (rather than hole) injection/passage is primarily responsible for the device degradation. Very high external Q.E. was demonstrated by Heeger et al. for the polymer **Comp. 14** blended with 20% of PBD (electron-transport material).⁶⁸ Increasing the operation temperature of the device from 25 to 85 °C, the $\Phi_{\text{EL}}^{\text{ext}}$ values increased from 2% to 4%. Comparing these numbers with the PL quantum yield (~8%), measured by exciting the material-incorporated diodes, the authors reached an interesting, though somewhat speculative conclusion that 50% singlet/triplet ratio is achieved in this material (which exceeds the widely-accepted theoretical value of 25%). A related enantiomerically pure (*S*)-2-methylbutoxy substituted PPV **Comp. 15** has been used to create circularly polarized PLED, in which the polarization is brought by molecular chirality of the polymer and does not require any molecular alignment.⁷⁷

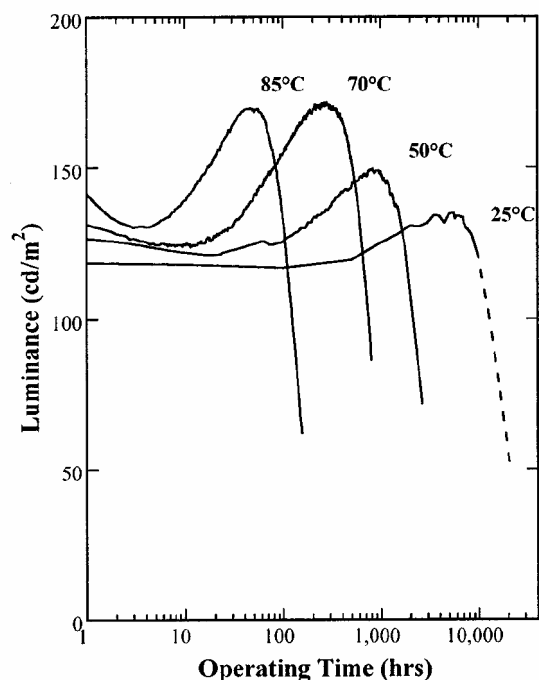


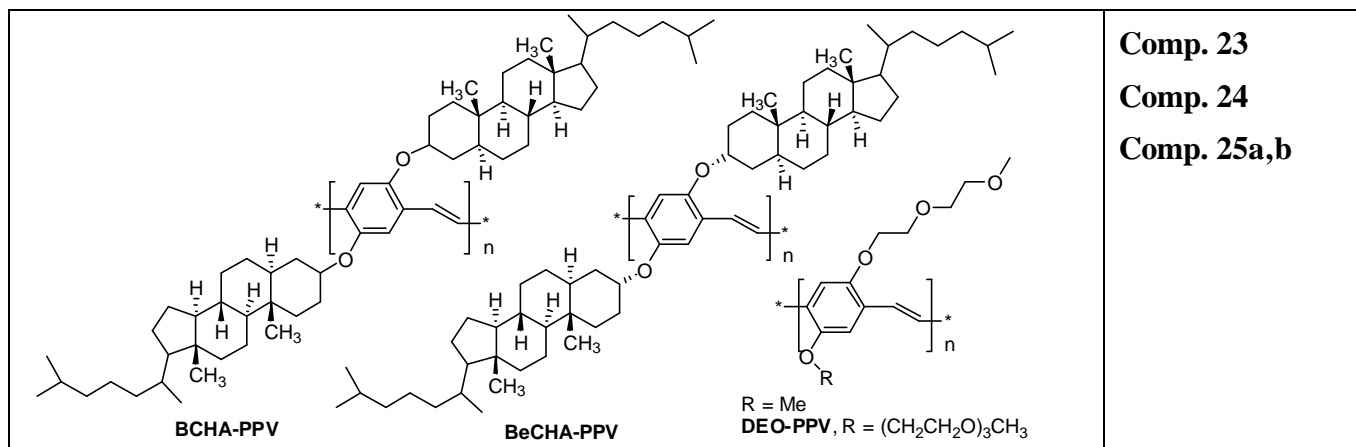
Figure 2. Operation life-time of the device ITO/PANI/**Comp. 14**/Ca/Al. [From Ref. 76, © 1999 American Institute of Physics].

Polymer **Comp. 16** bears two alkoxy substituents at positions 2 and 3 of the benzene ring, which showed notable blue-shifted absorption and emission bands ($\lambda_{\text{PL}} = 519$ nm, close to that of unsubstituted PPV) with ca. twice higher solid-state PL efficiency (40%) compared with 2,5-disubstituted PPVs (15-20%).⁷⁸ The EL efficiency of 0.03 cd/A (for Al cathode) and 0.07 cd/A (for Ca cathode) at 10-15 V operating voltage were reported for a single layer device, whereas in a double layer PLED with PPV **Comp. 1** as a hole-transporting layer, the high efficiency of 0.68 cd/A was achieved at 7.5 V (and maximal brightness of 4500 cd/m²). Notably, a similar polymer **Comp. 17** showed somewhat lower PL efficiency (28% vs. 40%), and the PLED device fabricated as ITO/PEDOT/**Comp. 17**/Ca showed the EL efficiency of 0.13 cd/A (and maximal brightness of only 86 cd/A).⁷⁹

Many other monoalkoxy-PPV (e.g. **Comp. 18a**⁸⁰) as well as symmetric (e.g., polymer **Comp. 18b**⁸¹ and **Comp. 19a**⁸²) and asymmetric (e.g., polymers **Comp. 19b-d**⁸³) dialkoxy-PPVs have been synthesized. Interestingly, the monoalkoxy-PPV **Comp. 18a** demonstrated improved PL quantum yield ($55\pm 5\%$), as compared to dialkoxy-PPVs, and the authors emphasize a key role of the synthetic conditions determining the photophysical properties of the polymer.⁸⁰

Electroluminescence from tetraalkoxy-substituted PPV **Comp. 20**, synthesized by Gilch polymerization, was recently reported.⁸⁴ A multi-layer device ITO/PEDOT/**Comp. 20**/PBD/LiF/Al with PBD as an electron transporting layer emits green-yellow light with luminescent efficiency 0.12 lm/W, maximum brightness 8,200 cd/m² and turn-on voltage of 5 V.

Probably, the most branched among the alkoxy-PPVs are cholestanoxo substituted polymers **Comp. 23**, **Comp. 24** developed by Wudl et al.^{81,85,86,87} The authors suggested that highly amorphous nature, possessed by all known steroids will result in highly soluble PPVs with very good film-forming properties. Indeed, the solid state fluorescence efficiency for **Comp. 23** was reported to be 53%, which is more than twice higher than that of MEH-PPV **Comp. 13** measured in the same conditions.⁸⁸ Oligoethylenoxy-substituted PPVs **Comp. 25**^{89,90} are also known, but the photoluminescence efficiency of these in the solid state is very low (0.6% for **Comp. 25a** and 8.8% for **Comp. 25b**⁹⁰), which is transmitted into low efficiency of PLED (ITO/**Comp. 25b**/Al: luminous efficiency 0.04 lm/W).

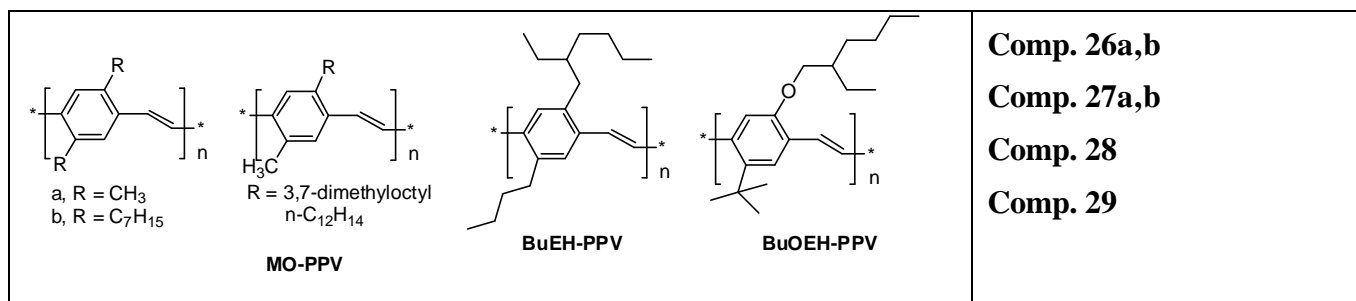


A combined theoretical (AM1, VEH) and experimental (UPS) study of the effect of alkyl/alkoxy substituents on the electronic structure of PPV has been undertaken by Fahlman, Brédas et al.⁹¹ The results suggest that strong influence of the substituents on the HOMO/LUMO levels (and the band gap) is primarily due to change in the torsion angle between the phenylene and vinylene groups. Interestingly, introduction of the alkoxy substituents does not cause significant steric hindrances, and weak intramolecular O... H interactions (between the oxygen atom of alkoxy group and a vinylic proton) in dialkoxy-substituted PPV may even favor the planar backbone geometry. In contrast, the dialkyl-substituted PPV is predicted to have a large torsion angle of 34° in the gas phase, and in the solid state the intermolecular packing and planarization will result in significant change of the band gap.

1.2.2. Alkyl substituted PPVs

A number of alkylated PPV polymers have been reported, e.g. **Comp. 26a**,^{57,82,92} **Comp. 26b**,⁹³ **Comp. 27**.⁹⁴ The absorption of dialkylated PPVs is very close to that of unsubstituted PPV **Comp. 1** [**Comp. 26b**: $\lambda_{\max} = 404 \text{ nm}$ ⁹³ (solution); **Comp. 28**: $\lambda_{\max} = 422 \text{ nm}$ (film)⁸⁸] and hypsochromically shifted in respect to dialkoxy-PPVs. It was demonstrated that dialkylated PPV **Comp. 28** can be used

as a new-type solid-state laser material.^{17,95} As for PLEDs, the first devices ITO/polymer/Ca fabricated with polymers **Comp. 27** emitted light with $\lambda_{\max} = 530\text{--}560\text{ nm}$, but the reported external Q.E. (0.2%) was lower,⁹⁴ comparing with alkoxy-PPV (**Comp. 13**) in same device configuration.⁶² Somewhat later very high Q.E. PLEDs have been fabricated with *t*-butyl/2-ethylhexoxy-PPV **Comp. 29**.⁶⁵ The device in configuration ITO/PANI/**Comp. 29**:surfactant/Al (where surfactant was lithium organophosphonate) emitted green light with external Q.E. as high as 2.7% (turn-on voltage 10 V), although this high value is mostly due to surfactant effect and a similar efficiency was obtained for MEH-PPV **Comp. 13** based device in the same configuration.



1.2.3. Silyl substituted PPVs

Several PPV derivatives possessing trialkylsilyl substituents have been studied with the aim to control the band-gap and the emission color of the polymer. The electronic influence of silicon substituent is somewhat difficult to predict. Judging from the variety of reported Hammett σ -constants of silyl substituent, it may act either as a weak electron donor or electron acceptor. Probably, more importantly in the case of substituted PPV, the bulky trialkylsilyl group increases the torsion angle between the phenylene and vinylene π -systems, thus enlarging the band-gap of the polymer. The first Si-substituted PPV **Comp. 30** was synthesized by Wudl's group.⁹⁶ Clearly, the trialkylsilyl substituent increases the band-gap, and shifts the emission into blue region: thin films of **Comp. 30** exhibit light green EL emission with an external Q.E. up to 0.3 %.⁹⁷

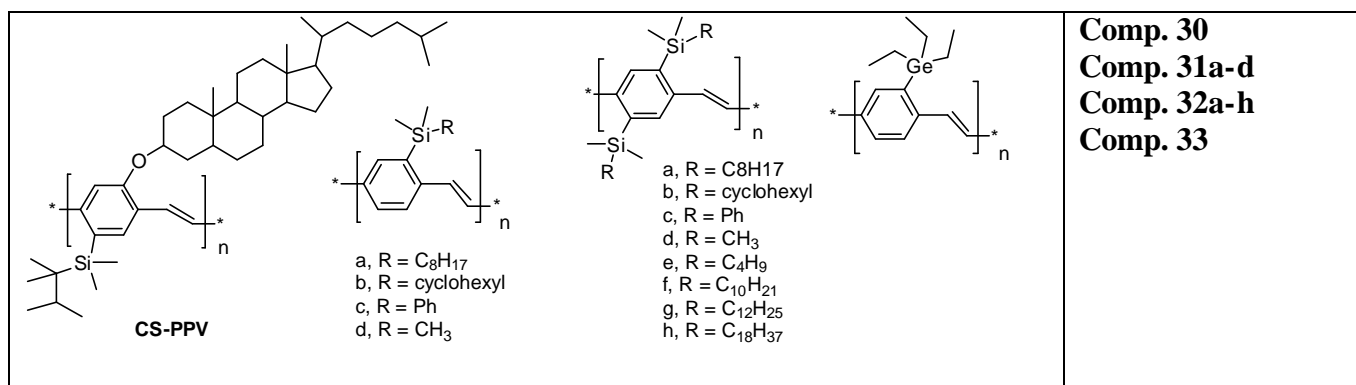
A simple Si-containing polymer **Comp. 31** has been later reported by Friend et al.⁹⁸ The optical band gap of this material in thin films is almost 2.5 eV, and it emits light at λ_{PL} 515 and 550 nm, with remarkable (as for PPV derivatives) PL quantum yield of 60%. A single layer PLED device reveals the same emission spectrum and the external Q.E. of 0.05 and 0.08%, for ITO/**Comp. 31**/Al and ITO/**Comp. 31**/Ca structures, respectively. The Q.E. can be significantly improved (to 0.2 and 0.5%, respectively), by introducing a hole blocking/electron injecting layer of PBD (in a blend with polystyrene) between the light-emitting layer and the cathode.

Holmes et al. studied silyl substituted PPVs **Comp. 31a**⁹⁹ and **Comp. 32a**¹⁰⁰ and their copolymers with 2,3-dibutoxy-PPV **Comp. 16**.⁷⁹ The solid state PL efficiency of **Comp. 31a** and **Comp. 32a** is over 60%, which is significantly higher than that of PPV **Comp. 1** (27%) and MEH-PPV **Comp. 13** (15%). Polymer **Comp. 31a** reveals bright green electroluminescence with external Q.E. of 0.05% (in ITO/**Comp. 31a**/Al configuration) and 0.1% (in ITO/**Comp. 31a**/Ca configuration).⁹⁹ Interestingly, the PLEDs made from **Comp. 32a** emit light at both positive and negative biases, but the EL efficiency was not reported.

A systematic study in a series of bis-silyl substituted PPVs **Comp. 32d-h** with different side chain lengths ranging from C1 to C18 was performed by Huang et al.¹⁰¹ The long-chain silyl-substituted PPVs show improved processability and film-forming properties, and sharp emission band, although the thermal stability of the polymer somewhat decreases for the longest chain substituents. The external Q.E. of the device built with Al cathode (ITO/**Comp. 32f**/Al) is not too bad (0.05%) as for

this diode structure, but, interestingly, only little improvement of the efficiency (to 0.08%) was observed when replacing the Al cathode with Ca.

To improve the mechanical properties and the thermostability of the silyl-substituted PPVs, Shim et al. replaced the long *n*-alkyl chains in silyl substituents with more sterically demanding cyclohexyl and phenyl groups (polymers **Comp. 31b**, **Comp. 32b**, and **Comp. 31c**, **Comp. 32c**, respectively).¹⁰² The best results (processability and EL efficiency) have been achieved for mono-substituted polymers **Comp. 31b** and **Comp. 31c**, which had high T_g (~ 125 °C), were thermally stable (5% mass lost at >430 °C), and, due to high molecular weight ($M_n \sim 3 \times 10^5$), possessed good film-forming properties. The PLED fabricated with these polymers as ITO/PVK/**Comp. 31c**/Al and ITO/PVK/**Comp. 31b**/Al emitted green-yellow light ($\lambda_{\max} \sim 520$ nm) with external Q.E. of 0.08% and 0.07%, respectively, and the maximal brightness of the device was also quite low (220 cd/m²).



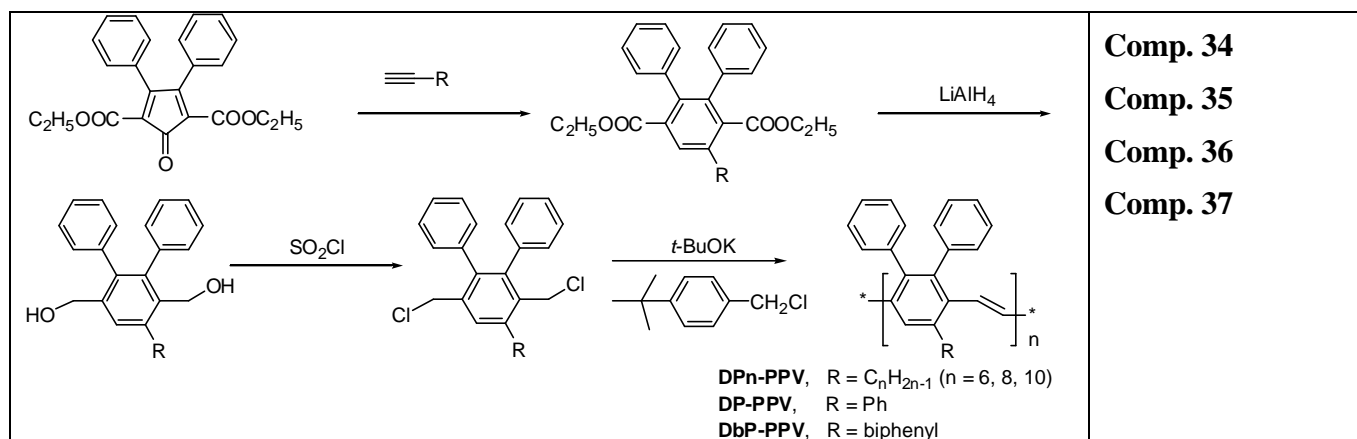
Recently, Hwang et al. reported the synthesis of germylated PPV **Comp. 33**.¹⁰³ Due to insolubility of the material, prepared by Gilch polymerization, the authors employed thermoconversion route to prepare thin films of **Comp. 33** from a non-conjugated methoxylated precursor polymer. The rational beyond this synthesis was to increase steric hindrances (due to bulkier germanium atom) and to prevent the interchain quenching effect, but no essential improvement vs. silylated analogues has been found. The device fabricated as ITO/**Comp. 33**/LiF/Al emitted green light ($\lambda_{\max} = 514$ nm) with efficiency of 0.015 lm/W and the maximal brightness of 600 cd/m² (cf. **Comp. 31d**:¹⁰³ efficiency 0.025 cd/W, brightness 310 cd/m²). The turn-on voltage (13 V) was even somewhat higher than that for silylated PPV **Comp. 31** (10.5 V).

Generally, silyl-substituents seem to retard the hole-transporting ability of PPV. As the result, devices fabricated from silyl-substituted PPVs suffer from a high turn-on voltage. To improve the EL efficiency PLEDs fabricated by Si-PPVs, the introduction of additional hole injection layer or co-polymerization with electron-rich co-monomers is required.

1.2.4. Aryl substituted PPVs.

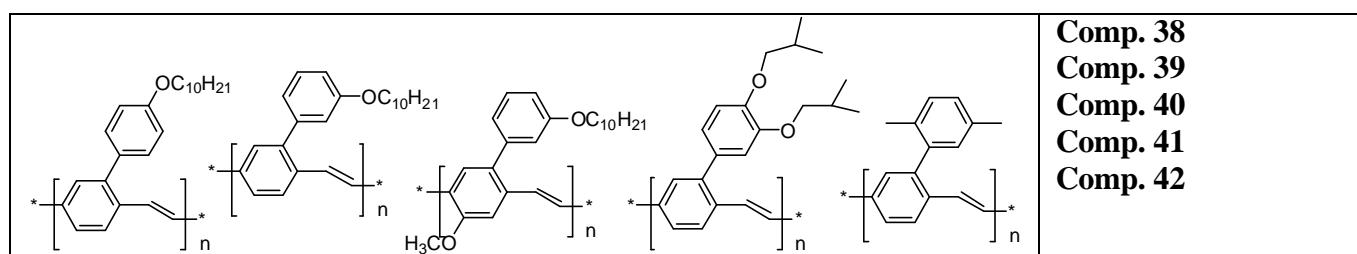
A numerous studies have been devoted to PPV derivatives possessing pendant aromatic groups. In 1998 Hsieh et al. synthesized a series of soluble diphenyl PPV derivatives, via indigenous route based on a Diels-Alder reaction of commercially available substituted cyclopentadienone with alkylacetylenes (Scheme 12).¹⁰⁴ This is a very versatile method for preparation of a variety of substituted monomers for PPV. In contrast to a classical route of chloromethylation of alkyl (alkoxy) substituted benzenes, the Diels-Alder approach eliminates a problem of isomers formation. The polymerization of the monomer **Comp. 34** was carried out either through the chlorine precursor route for insoluble polymers **Comp. 36** and **Comp. 37** or via modified Gilch route involving the end-capping

with 4-tert-butylbenzyl chloride for **Comp. 35**. However, even with the later, the extremely high molecular weight of the polymer (M_w exceeds 2×10^6 for 1: 0.05 ratio, 4×10^5 for 1:1 ratio) was still an issue affecting the material processability (which, though, is also the case for MEH-PPV **Comp. 13**). Due to significant steric factors of this substitution pattern, the emission of polymer **Comp. 37** is blue-shifted to a $\lambda_{\max} = 490$ nm, which is very low as for fully conjugated PPVs. Furthermore, the solid state PL efficiency also reached a very high value of 65%, which can be explained by preventing the intermolecular quenching in highly distorted polymer chain material.



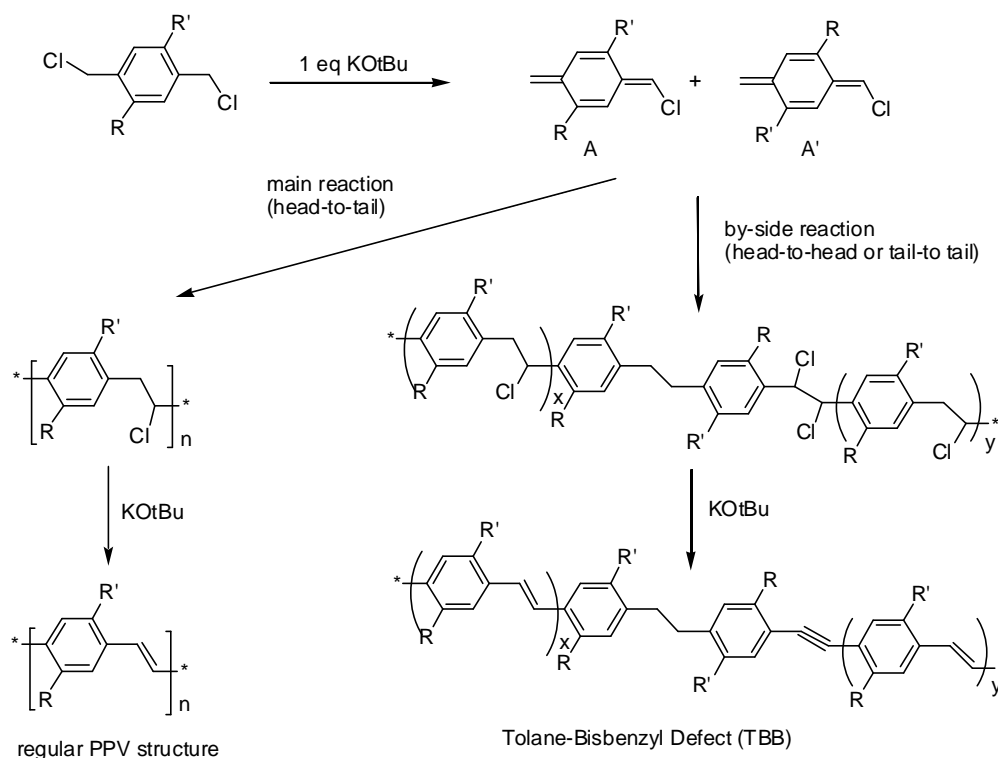
Scheme 12. Synthesis of 2,3-diphenyl substituted PPVs.

The solubility of the phenyl-PPVs can be greatly improved by introduction of alkoxy-substituents into pendant phenyl group. Spreitzer, Becker et al. first reported the alkoxyphenyl substituted PPVs **Comp. 38–Comp. 42** and their numerous co-polymers (see below) prepared through a modified Gilch route.^{105,106} These polymers exhibited high PL quantum efficiency and PLED fabricated using these alkoxy-substituted phenyl PPVs showed improved EL performance owing to their good film-forming properties. Thus, the green-emitting PLED ITO/**Comp. 39**/Ca demonstrates the external Q.E. of 3.1% (7.9 cd/A).^{106,107}



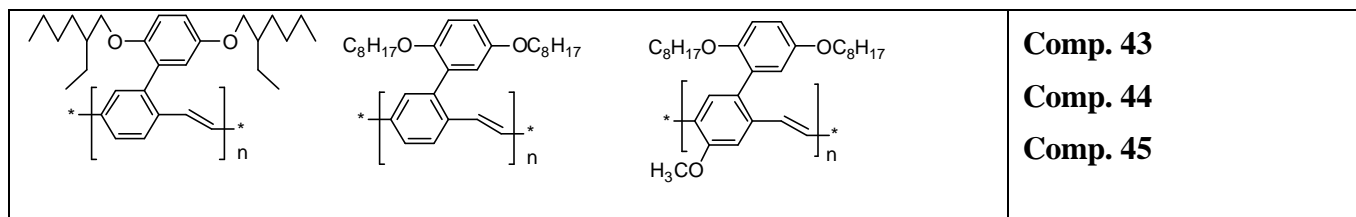
However, later, it was found that the phenyl-substituted PPVs have a significant level of defect structures tolane-bisbenzyl (TBB) moieties built in the polymer chain.¹⁰⁶ The defects have moderate influence on the polymer photophysical properties but strongly affect the PLED device life-time. In fact, the amount of TBB defects in phenyl-substituted PPVs is several times higher than in similarly prepared dialkoxy-PPVs (5–6 % in Ph-PPV vs. 1.5–2.2% in dialkoxy-PPVs **Comp. 13** or **Comp. 14**). Considering the mechanism of TBB formation (Scheme 13), the monophenyl-substituted monomers should favor such defects. Due to similar acidity of both CH_2Cl groups two types of quinone intermediate, A and A', can be formed. In the same time, the steric hindrances brought by Ph group will favor the head-to-head coupling of these monomers, rather than a normal head-to-tail reaction. The

amount of TBB defects can be significantly suppressed (to <0.5%) by introducing an additional methoxy substituents into phenyl-PPV monomer. This is especially important, as it has been shown that the lifetime of the phenyl-substituted PPVs in PLED is increased by over 30 times on lowering the TBB content from 6 % to 3 %.¹⁰⁶



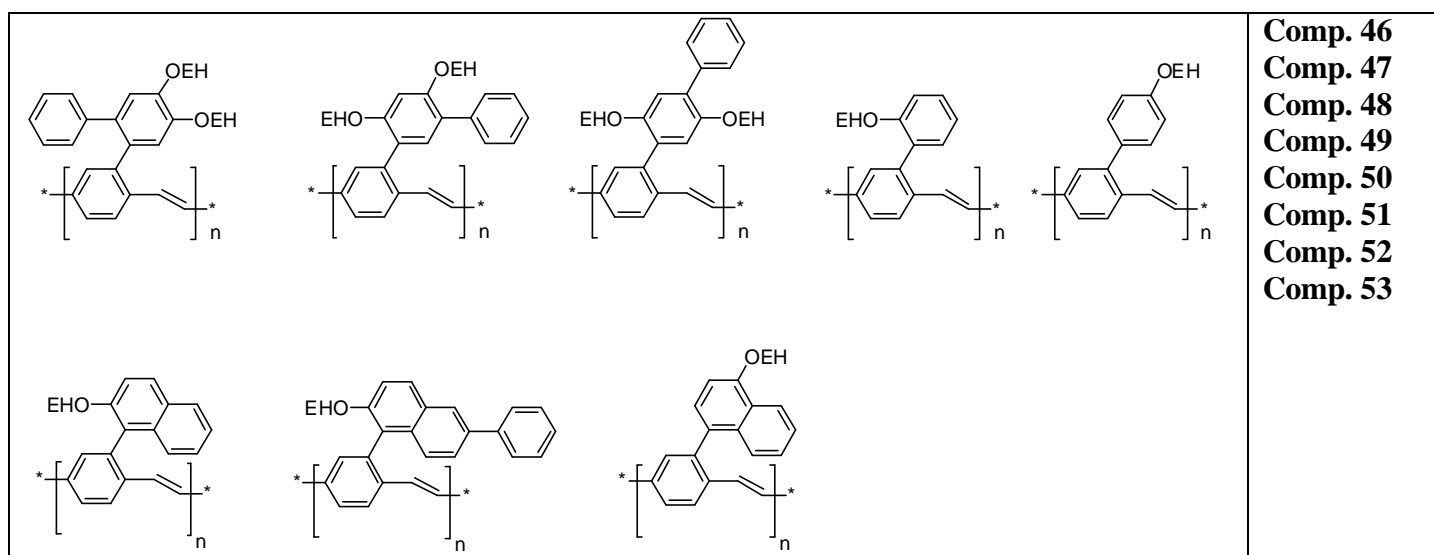
Scheme 13. The mechanism of formation of TBB in the Gilch polymerization.¹⁰⁶

Introducing two alkoxy substituents in positions 2,5 of the phenyl side group can efficiently prevent the interchain fluorescent quenching, as has been demonstrated in polythiophene series.¹⁰⁸ Based on this observation, Andersson et al. synthesized phenyl-substituted PPVs **Comp. 43** and studied its properties and electroluminescent performance.^{40,109} As in other phenyl-substituted PPVs, the TBB defects was a major problem, although the amount of defects can be somewhat decreased by careful control of the reaction conditions: the TBB content of 9% for the polymer prepared at 144 °C reduces to 3% for the polymer prepared at 0 °C. The highest external Q.E. (0.94%) was achieved with the polymer, prepared at 66 °C (in the PLED ITO/PEDOT/**Comp. 43**/Ca). The same group has also synthesized similar polymers **Comp. 44**, **Comp. 45**.¹¹⁰ As found earlier, the introduction of the alkoxy group in the phenyl-PPV backbone decreases the amount of TBB content. **Comp. 45** showed few times lower level of TBB defect compared with **Comp. 44**, and, performing the reaction at -35 °C, the amount of TBB can be brought below 1%. This difference is clearly reflected in the PLED device performance. The external Q.E. of PLEDs fabricated as ITO/PANI/polymer/Ba/Al is similar for both polymers (1.74 % for **Comp. 45** and 1.34 % for **Comp. 44**), but the operation life-time of the low-TBB content polymer **Comp. 45** is prolonged by ca. 5 times.



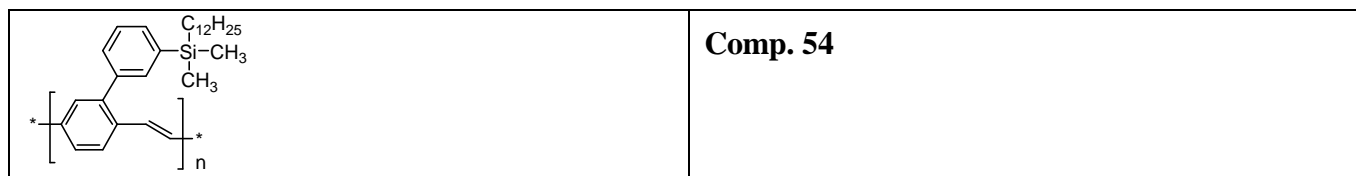
Recently, Chen et al. synthesized a series of dialkoxybiphenyl-substituted PPV polymers **Comp. 46–Comp. 48** and model alkoxyphenyl-PPVs **Comp. 49, Comp. 50** by Gilch route.¹¹¹ Additional phenyl rings were introduced in the side chain in order to investigate the effect of the steric interaction on the formation of TBB defects as well as to increase the thermal stability of the polymers. The authors describe the observed variation of TBB defect (~0.5% for polymer **Comp. 46** and ~4% for **Comp. 47** and **Comp. 48**) as “expected”, although the influence of the structural variations between, e.g., **Comp. 46** and **Comp. 47** is not obvious. The authors also demonstrated that using a more polar solvent as THF during polymerization helps to suppress the TBB formation by a factor of two, as compared to *p*-xylene. These results argue the previous finding by Andersson et al. who ascribed the suppression of the TBB formation in THF vs. *p*-xylene solution solely to the lower temperature, employed for the former.⁴⁰ The green-emitting PLEDs fabricated in configuration ITO/PEDOT/Polymer/Ba/Al showed the lowest turn on voltage for polymer **Comp. 46**, although the highest quantum efficiency 0.66 % was achieved for **Comp. 47** (0.37 % for **Comp. 46** and 0.25 % for **Comp. 48**).

Employing similar polymerization conditions (t-BuOK in THF at room temperature) in synthesis of naphthyl-substituted PPVs **Comp. 51–Comp. 53**, reported by the same group recently, the TBB defects can be brought below the NMR detection limit.¹¹² Although the absorption and PL spectra of all three polymers are similar, the electroluminescence can be finely tuned between 486 nm (for **Comp. 52**) and 542 nm (for **Comp. 53**). The external Q.E. (studied for ITO/PEDOT/polymer/Ba/Al device) is also sensitive to the substituents pattern in the naphthyl pendant group: 0.08% for **Comp. 51**, 0.02% for **Comp. 52** and 0.54% for **Comp. 53**.

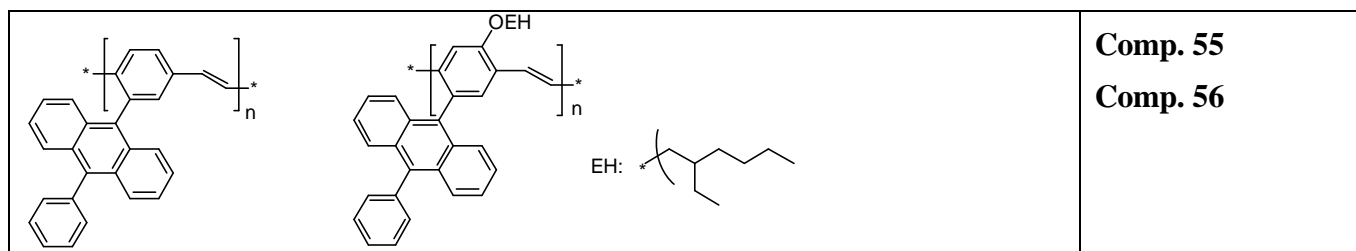


Jin et al. attached a solubilizing trialkylsilyl substituent in meta-position of the pendant phenyl group.¹¹³ The target polymer **Comp. 54** was purified by membrane dialysis and revealed improved thermal ($T_{\text{dec}} = 406\text{ }^{\circ}\text{C}$) and color stability. The device fabricated as ITO/PEDOT/polymer/Al:Li emits

light at $\lambda_{\text{max}} = 525$ nm with rather moderate performance: the maximum external Q.E. of 0.08%, the maximal brightness of 570 cd/m² (at 43 V), and the turn-on voltage as high as 14 V. The authors explained these discouraging results by a high energy barrier between the HOMO band of the **Comp. 54** (−5.30 eV) and the ITO/PEDOT workfunction (−5.0 V), although 0.3 eV barrier can hardly be the only problem with the device. Nevertheless, the device performance was significantly improved by co-polymerization with MEH-PPV **Comp. 13**, which raises the HOMO and also unexpectedly brings down the LUMO level of the co-polymer (see the Co-polymers section).



Earlier, the same group reported introduction of chromophoric 9-phenylanthracene substituents into the phenylene units of the PPV backbone: polymers **Comp. 55** and **Comp. 56** have been synthesized by Gilch polymerization route.¹¹⁴ The long-wavelength absorption of these polymers is blue-shifted (compared to PPV and MEH-PPV) due to twist in the polymer chain caused by steric influence of anthracene substituents: band gaps determined from the UV absorption onsets were 2.58 eV and 2.38 eV for **Comp. 55** and **Comp. 56**, respectively. Due to presence of two luminophores with different emission properties (alkoxy-PPV and anthracene) **Comp. 56** showed a very broad emission band (both in PL and EL, Figure 3). The EL efficiency of PLEDs fabricated in the configuration of ITO/polymer/Al increased in the order PPV **Comp. 1** < MEH-PPV **Comp. 13** < **Comp. 55** < **Comp. 56**, with efficiency for the last being almost 10 times higher than that of PPV **Comp. 1** at the same current.¹¹⁴ The authors assume a synergistically enhanced effect of the phenylanthracene and alkoxy substituents. Also, sterically bulky anthracene group may suppress the interchain interaction, thus increasing the EL efficiency.



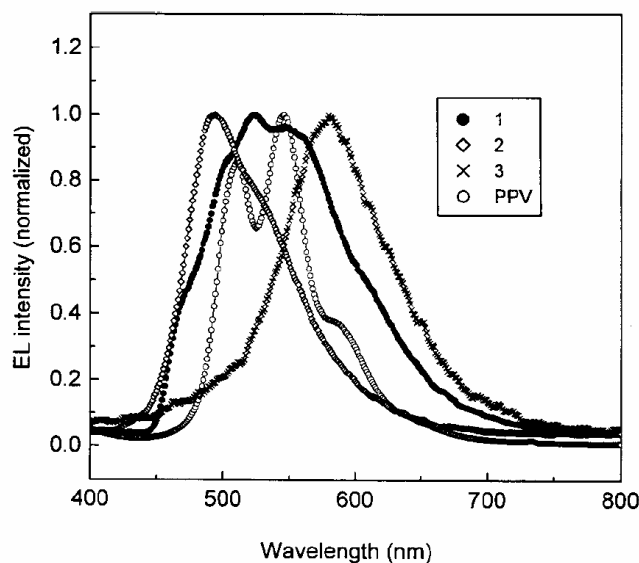
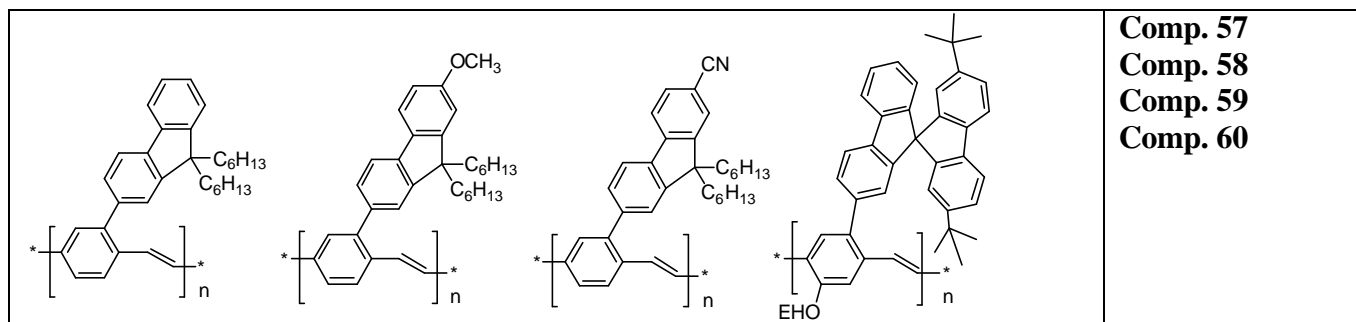


Figure 3. Electroluminescent spectra of PLEDs ITO/polymer/Al. 1 – **Comp. 56**, 2 – **Comp. 55**, 3 – MEH-PPV **Comp. 13**, PPV – **Comp. 1**. [From ref. 114, © 1998 Wiley-VCH].

An important extension to phenyl-substituted PPVs was first reported by Tsutsui et al. who used Gilch polymerization to synthesize fluorenyl-substituted PPVs (**Comp. 57**, **Comp. 58**, **Comp. 59**) and studied their performance in PLEDs.¹¹⁵ Due to bulky but rigid fluorene substituents, these polymers have excellent solubility and yet are thermally stable up to 320 °C and have the T_g of 113–148 °C. The electron donating methoxy group or electron withdrawing cyano group were introduced to adjust the optical and electronic properties of the polymers. However, the influence of the substituents in the fluorene nucleus on the redox and fluorescent properties of polymers **Comp. 57–Comp. 59** was found to be very small, indicating that PPV backbone rather than the pendant fluorene unit determines the optoelectronic properties of the system. In the same time, as was shown later, the substituents in fluorene nucleus retard the hole mobility of the polymer.¹¹⁶ In fact, the unsubstituted polymer **Comp. 57** showed quite high hole mobility of $4.5 \times 10^{-4} \text{ cm}^2/\text{Vs}$ (at electric field of $2.5 \times 10^5 \text{ V/cm}$), which is 2 orders of magnitude higher than that of MEH-PPV **Comp. 13**.

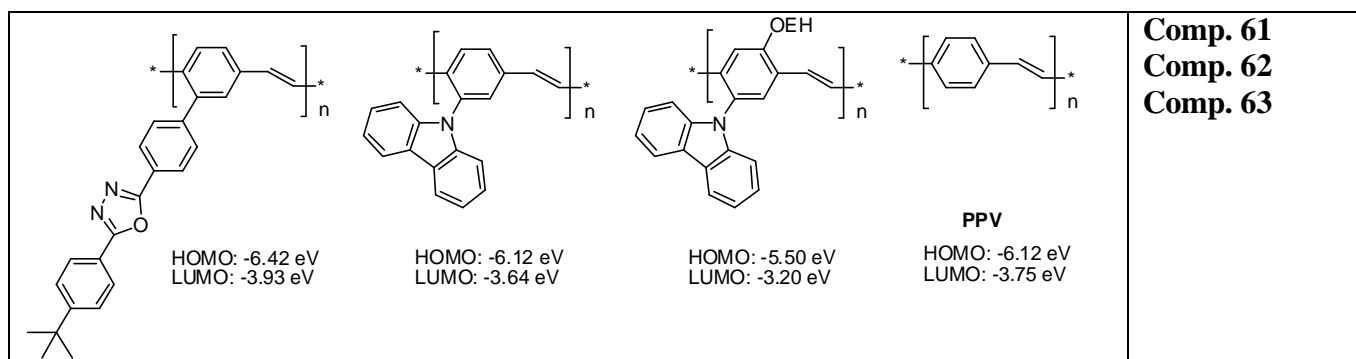
All three polymers emit blue green light with a maximum around 500 nm and a shoulder of 532 nm, with PL quantum yield of 68–71% (in solution). The PLEDs were fabricated with polymers **Comp. 57**, **Comp. 58** and **Comp. 59** as ITO/PEDOT/polymer/Ca. The EL performance of the device fabricated with **Comp. 57** had the lowest turn-on voltage (2.8 V) and the highest luminescence efficiency (a maximum luminance of $12,000 \text{ cd/m}^2$, with a maximum external Q.E. of 0.53 %). The performance of other two polymers **Comp. 58** and **Comp. 59** was similar, but the Q.E. was 1.6–2.8 times lower than that of **Comp. 57**. More recently Kwon et al. synthesized even more hindered spirobifluorenyl-PPV **Comp. 60**.¹¹⁷ **Comp. 60** is a highly soluble polymer with T_g as high as 200 °C, although its solid state PL efficiency is not very high (26%). The PLED showed a turn on voltage of 6 V and a maximum brightness of $1,150 \text{ cd/m}^2$ at 12.5 V and a maximum power efficiency of 0.12 lm/W.



1.2.5. Electron withdrawing/donating groups substituted PPVs.

One of the problems of application of conjugated polymer LEDs is rather high-lying LUMO energy level, which requires an unstable low work-function metal electrodes (as Ca) for efficient electron injection. The valence effective Hamiltonian calculations predict that introduction of an electron-withdrawing group onto either the phenyl ring or the vinyl unit of PPV lowers the HOMO and LUMO energies of the polymer.⁹¹ Significant improvement of the EL efficiency can be achieved by blending dialkoxy-PPV polymers with electron-transporting materials (as PBD).⁶⁸ In this regards, Jin et al.,¹¹⁸ compared the properties of PPV polymers carrying an electron-acceptor 2,5-diphenyl-1,3,4-oxadiazole group (resembling PBD, a widely used electron-transporter) and an electron-donor carbazole group (an excellent hole-transporter) (Scheme 14). In spite of absence of long solubilizing substituents, polymers **Comp. 61** and **Comp. 62** are very soluble in common organic solvents, probably due to relatively low molecular weight ($M_n = 24,000$ and $16,000$, respectively). Although the absolute efficiencies of the derived PLEDs was quite low (external Q.E. $< 0.004\%$) due to unoptimized device structure (ITO/polymer/Al), there is a clear dependence of the EL efficiency on the molecular orbitals levels: the lower was the barrier between the Al work function (-4.3 eV) and the LUMO of the polymer, the higher efficiency was achieved: **Comp. 61** $>$ **Comp. 1** $>$ **Comp. 62** (Scheme 14). This suggests that the electron/hole injection (or transport) in PPV is unbalanced, and holes are the dominant charge carriers.

On the other hand, in a later publication same group admitted that the charge injection barrier is not the only consideration playing role in maximizing the EL efficiency.¹¹⁹ Surprisingly enough, the introduction of a donor alkoxy substituents into carbazole-PPV, which further raises the LUMO level (but also brings down the HOMO and thus facilitates the hole injection) increases the EL efficiency. The same structure PLED, prepared with polymer **Comp. 63** possesses 550-fold external Q.E. (0.01%) as compared to polymer **Comp. 62**. Furthermore, a very high performance PLED can be fabricated with PEDOT-modified anode: the device ITO/PEDOT/**Comp. 63**/Ca/Al shows the EL efficiency of up to 4.4 cd/A and the maximal brightness in excess of $30,000$ cd/m².¹¹⁹ The device half-life time was estimated to be 70 h at brightness of $1,000$ cd/m².

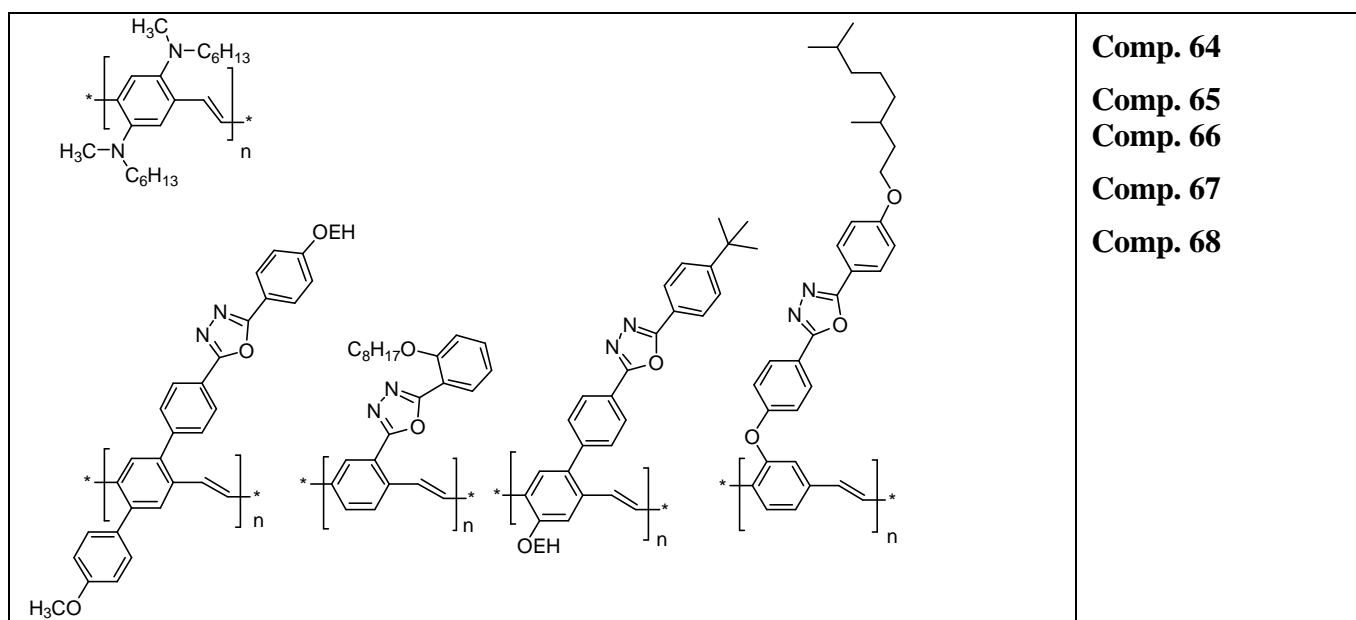


Scheme 14. Tuning the energy levels of PPV by introducing pendant charge-transporting units. The HOMO defined as the $-I_p$ value (determined from the UPS experiments) and the LUMO was deduced by adding the optical gap to the HOMO value.

In a similar approach, the HOMO level of PPV was controlled by introduction of dialkylamino donor group (**Comp. 64**).¹²⁰ The dialkylamino groups render the material high solubility and good film-forming properties, and, similar to alkoxy groups, shifts the emission maxima (~ 560 nm) in the red. The PLED ITO/**Comp. 64**/Mg/Al showed moderate efficiency (0.3% at ~ 30 cd/m²; 0.2% [0.45 cd/A, 0.08 lm/W] at 300 cd/A), but the turn-on voltage (>10 V) was rather high.¹²⁰

Balancing the charge transport via introducing electron-transporting oxadiazole groups was further developed by Huang et al. who synthesized the polymers **Comp. 65** and **Comp. 66** by Gilch polymerization.^{121,122} Surprisingly, the polymer **Comp. 65** was completely insoluble, regardless of preparation conditions (Gilch polymerization), which was explained by its very rigid-structure.¹²¹ This is in drastic contrast with **Comp. 61**, which does not even have long-chain 2-ethylhexyloxy substituents, and can be due to higher molecular weight. Polymer **Comp. 66**, where the *o*-alkoxyphenyl-substituted oxadiazole nucleus is directly connected to the PPV backbone, is a highly soluble material with moderate molecular weight of $M_n = 20,700$ and rather high T_g of 170 °C. The PLEDs fabricated with this polymer in simple ITO/polymer/Al configuration showed improved charge transport properties, as seen from the low turn-on voltage (4.0 V), at which the device starts to emit a yellow-orange light.

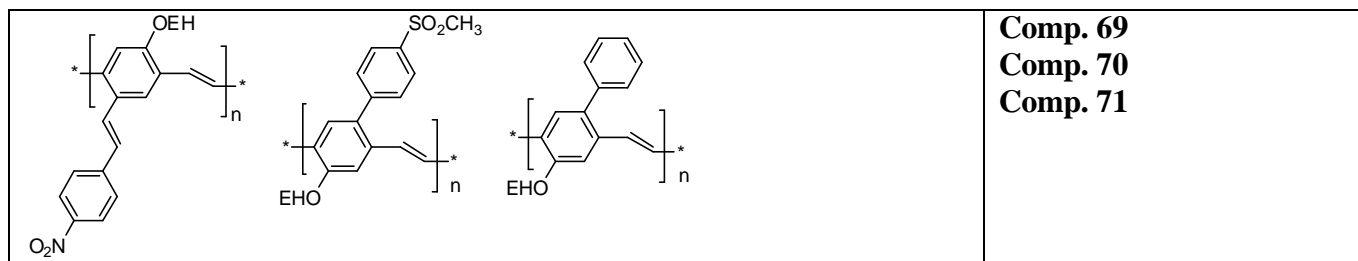
Jin et al. synthesized PPV **Comp. 67** containing an oxadiazole and an alkoxy groups.¹²³ According to UPS study, the HOMO and LUMO levels in **Comp. 67** (-6.32 and -3.98 eV) are lowered versus those in the parent polymer **Comp. 61** without alkoxy substituents (Scheme 14), which suggests an unexpected electron-withdrawing effect of the alkoxy substituent in this system. The external Q.E. of PLEDs based on polymer **Comp. 67** is about one order of magnitude higher than that for **Comp. 61** (0.045% for ITO/**Comp. 67**/Li:Al) and the maximal brightness of up to $7,570$ cd/m² was achieved for this material (using Ca cathode).



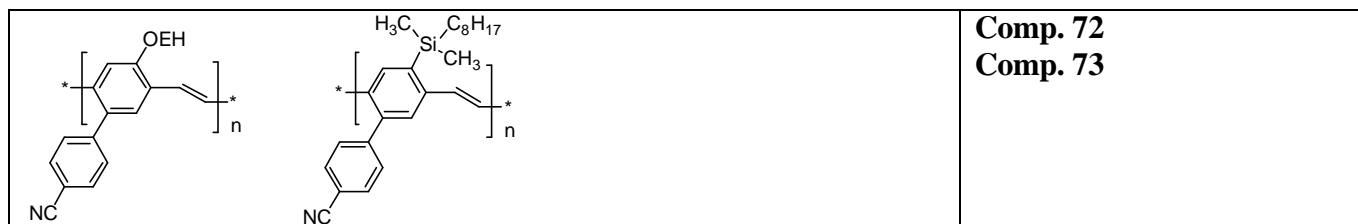
The recently synthesized PPV **Comp. 68**, in which the oxadiazole group is separated from the PPV backbone by an oxygen atom, is a very soluble material with optical band-gap 2.36 eV and

yellowish-orange emission color (CIE: $x = 0.50$, $y = 0.47$; $\lambda_{\text{max}}^{\text{PL}} = 591 \text{ nm}$).¹²⁴ Extremely high performance PLEDs was claimed for this polymer in a single-layer configuration (ITO/PEDOT/**Comp. 68**/Al). The device is characterized by a low turn-on voltage of 5 V, achieves the maximum brightness of 19,400 cd/m^2 at 14 V, and demonstrates the luminance efficiency of 21.1 cd/A (at 5,900 cd/m^2), which ranks it among the best performing electroluminescent PPV materials.

Using chlorine precursor route, Burn et al. introduced several electron accepting moieties, such as p-nitrostyryl (**Comp. 69**)¹²⁵ and methylsulfonyl-phenyl (**Comp. 70**)¹²⁶ groups as substituents in PPV backbone. However, essentially no difference in EL performance (maximal Q.E. 0.01 % for ITO/polymer/Al) was found between polymers **Comp. 70** and **Comp. 71**, and the authors conclude that the methylsulfonyl group in the pendant phenyl ring does not facilitate the electron injection.

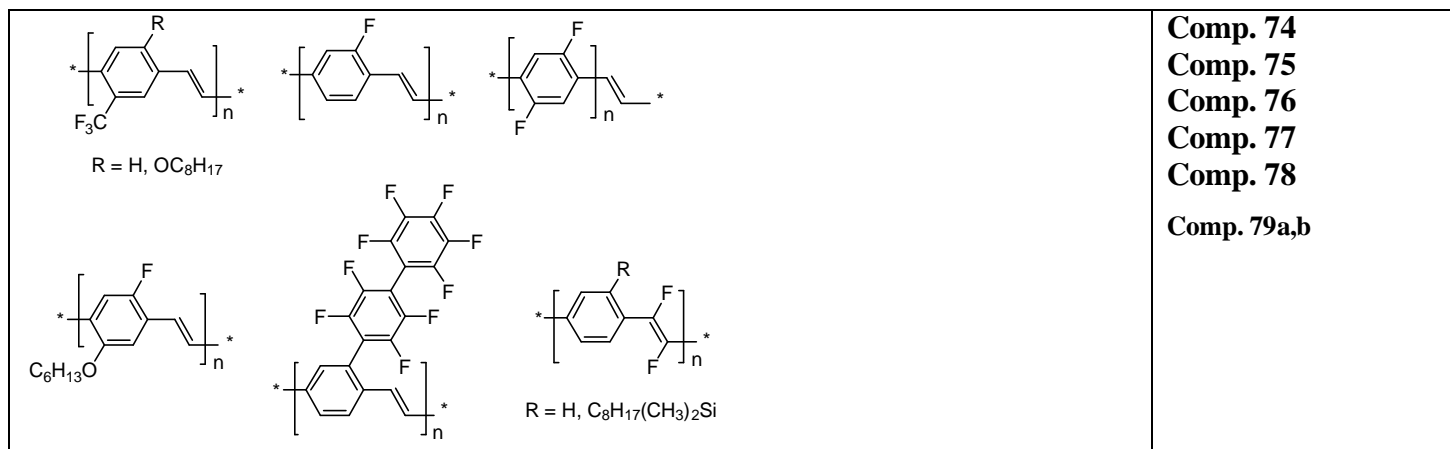


Similar materials, containing electron withdrawing cyano groups, also attached to pendant phenyl substituents, were recently synthesized by Shim et al. via Gilch polymerization.¹²⁷ The polymers **Comp. 72** and **Comp. 73** are soluble in organic solvent, show good thermal stability (less than 5% weight lost at 400 °C) and very high T_g (192 and 180 °C, respectively). The PL quantum efficiencies of **Comp. 72** and **Comp. 73** were 43% and 62%, respectively. PLEDs fabricated in ITO/PEDOT/polymer/LiF/Al configuration emitted greenish-yellow light (CIE: $x = 0.455$, $y = 0.532$) for **Comp. 72** and very pure green light (CIE: $x = 0.330$, $y = 0.599$) for **Comp. 73**, which is very close to the standard green color (CIE: $x = 0.30$, $y = 0.60$) used in high definition television (HDTV). According to electrochemical measurements, both polymers possess similar LUMO energy values (−2.72 eV for **Comp. 72** and −2.75 eV for **Comp. 73**, respectively), but their HOMO energy levels are different (−5.41 eV for **Comp. 72** and −5.72 eV for **Comp. 73**), reflecting the difference in electron-donating properties of alkoxy and trialkylsilyl substituents (and also steric factor of the trialkylsilyl substituent, reducing the conjugation). Interestingly, the HOMO energy level of **Comp. 72** is closer to the work function of PEDOT (−5.0 eV), but its EL performance is lower: the maximum brightness of **Comp. 73** is 2,900 cd/m^2 at 10 V (maximal Q.E. 0.65%), whereas polymer **Comp. 72** reaches only 330 cd/m^2 at 10.5 V (maximal Q.E. 0.025%). Once again, these results indicate on a not well-understood, yet very beneficial effect of silyl substituents on the electroluminescent properties of PPV polymers.



Several groups have investigated the effect of fluorine electron-withdrawing substituents in PPV. The trifluoromethyl electron-withdrawing group (polymer **Comp. 74**) attached directly to the phenylene units improves the electron injection quite significantly, but, probably, also acts as a

quencher: the PL quantum yield of this polymer (5–7 %) is much lower than that of parent PPV (27%).¹²⁸ As a result, single layer LED devices ITO/**Comp. 74**/Al and ITO/**Comp. 74**/Ca showed almost the same external Q.E., which was one order of magnitude lower than that of ITO/PPV **Comp. 1**/Ca.



Shim et al. synthesized the poly(2-fluoro-1,4-phenylenevinylene) **Comp. 75** by thermal conversion method.¹²⁹ This polymer have almost the same absorbance spectra as PPV **Comp. 1** ($\lambda_{\text{max}} \sim 410$ nm), but the fluorescence band ($\lambda_{\text{max}} = 560$ nm) is red-shifted by *ca.* 20 nm. The LUMO level was shifted down by *ca.* 0.15 eV, facilitating the electron injection, but, in contrast to the above polymer **Comp. 74**, no fluorescence quenching was observed. Consequently, the PLED device fabricated as ITO/**Comp. 75**/Al have *ca.* 10 times higher EL efficiency than that fabricated with PPV **Comp. 1** under identical conditions.

Comparative analysis of different fluorine-substituted PPVs **Comp. 75–Comp. 77** has been performed by Karasz et al.¹³⁰ Polymers **Comp. 75** and **Comp. 76** exhibit blue-shifted UV absorbance relative to PPV **Comp. 1**, but, remarkably, have substantially red-shifted PL and EL emissions bands. In push-pull polymer **Comp. 77** both the absorption and emission maxima are red-shifted relatively to **Comp. 1**. The LED performance of these materials appeared to be rather low (the EL efficiency of ~ 0.002 cd/A and the maximal luminance of ~ 100 cd/m² was achieved at 30 V), and the turn-on voltage for the push-pull polymer **Comp. 77** (4 V) was lower than that in more electron deficient polymers **Comp. 75** and **Comp. 76**.

Jang et al. reported high electron affinity perfluorobiphenyl-substituted PPV **Comp. 78**.¹³¹ This polymer was synthesized by the thermoconversion method. Single layer PLED ITO/ **Comp. 78**/Al showed 64 times higher EL efficiency than that fabricated with unsubstituted PPV **Comp. 1**. A further (380-fold) increase of efficiency was achieved in bilayer device ITO/**Comp. 1**/**Comp. 78**/Al.

Fluorine has also been introduced into vinylene fragment of PPV (**Comp. 79a,b**).¹³² Blue shifts of absorption were observed for these polymers when hydrogen in the phenylene ring is substituted by silyl group [from 580 to 495 nm for PL and from yellow to green EL emission (from 565 to 540nm)]. The turn-on voltage of ITO/PEDOT/**Comp. 79**/Al devices was 3–4 V and silyl-substituted polymer showed the maximum luminance of 2.7 cd/A at 6.5 V and maximum brightness of 750 cd/m² at 7.5 V that is *ca.* 7 times higher than for non-fluorinated analog.

Chlorine substituents have also been introduced into PPV (in phenylene units), but no EL or PL properties of these materials have been reported.⁵⁷

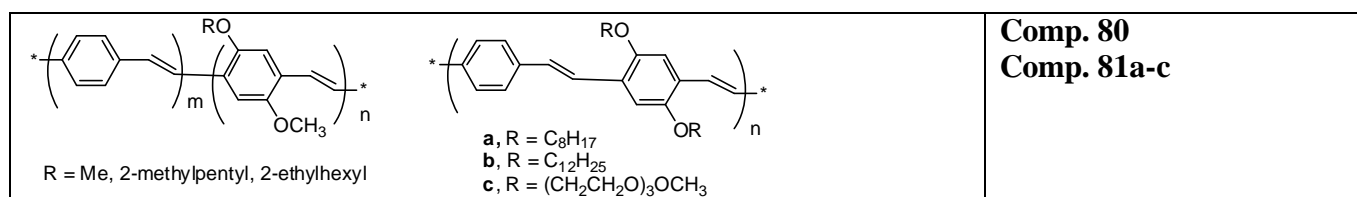
1.3. Conjugated PPV co-polymers

1.3.1. PPV co-polymers with electron donor and aryl substituents.

Due to higher variety of possible structures, co-polymers allow a better control of the HOMO/LUMO levels, necessary to optimize the EL properties of PPV, as compared to homopolymers. Often, the optical and electronic properties in co-polymers can be finely tuned by simple changing the feeding ratio of co-monomers (although the structure-properties relationship in these systems is even more complex than in homo-PPV polymers). Using different co-monomer units, various PPV-based materials with tuned optical and electronic properties have been prepared.

Although MEH-PPV **Comp. 13** (at a time of discovery) was one the most efficient soluble polymers for PLEDs application, its performance is not high enough for commercialization as LEP. One of the reasons is unbalanced hole/electron mobility in MEH-PPV (the mobility of holes is 100 times faster than the mobility of electrons).¹³³ Copolymerization with other conjugated monomers, to some extent, can improve the electron-transporting properties and increase the EL performance.

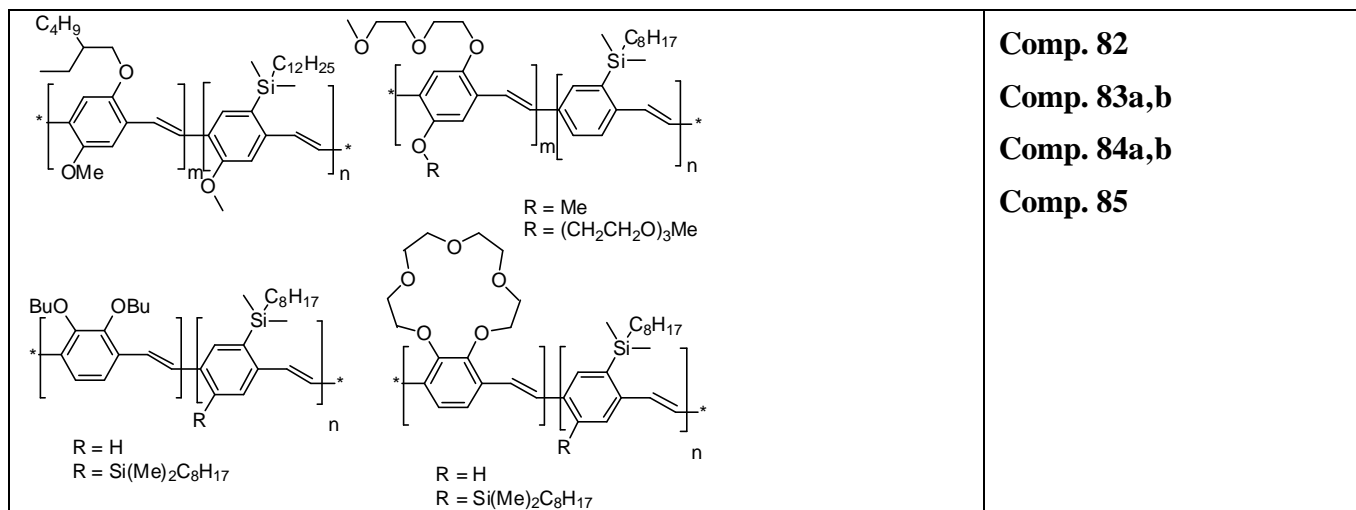
The first realization of this approach has been reported by the Cambridge group, which synthesized co-polymers **Comp. 80** containing (phenylene vinylene) and dialkoxy (phenylene vinylene) units by thermoconversion method.^{23,134} The 30 fold improvement in EL efficiency was observed for these co-polymers compared with PPV **Comp. 1** or MEH-PPV **Comp. 13** devices fabricated in the same configuration.



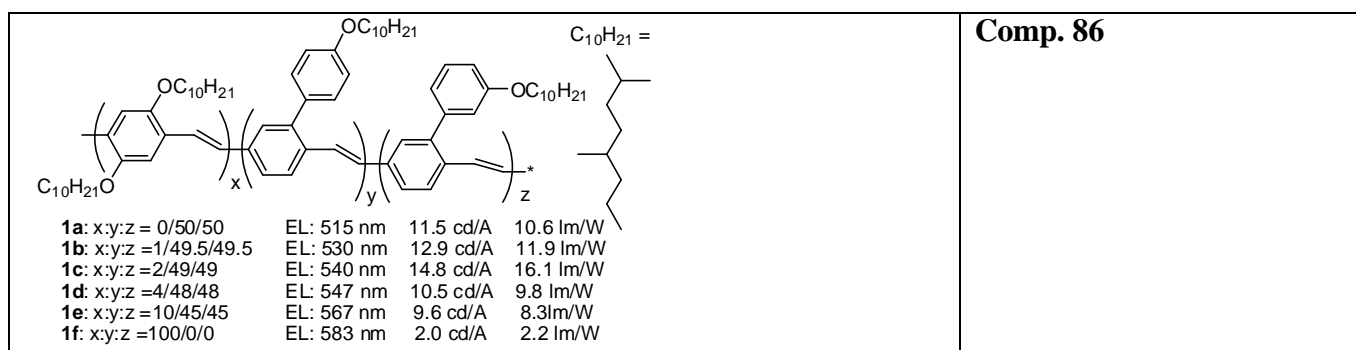
Since then, most research groups use the co-polymerization approach to tune the properties of EL materials. The synthetic methods include the Wittig-Horner condensation, Gilch polymerization, Heck's reaction, etc. A number of PPV co-polymers similar to **Comp. 80** was synthesized (e.g., **Comp. 81a**,¹³⁵ **Comp. 81b**¹³⁶). Most recently, Huang et al. used a Wittig-Horner reaction to construct the polymer **Comp. 81c** with hydrophilic oligoethyleneoxy substituents for LECs.¹³⁷ This co-polymer is a yellow-green emitter, which efficiency can be improved from 0.038 lm/W (in classical LED configuration ITO/polymer/Al) to 0.185 lm/W (in LEC ITO/polymer+LiOTf/Al).

The groups of Holmes and Friend reported a series of PPV co-polymers containing alkoxy and trialkylsilyl substituted phenylene rings in random distribution (**Comp. 82–Comp. 83**,⁹⁰ **Comp. 84**,⁷⁹ **Comp. 85**¹³⁸). The authors mention that introduction of the trialkylsilyl group results in *ca.* 5-time increase of the luminous efficiency of co-polymers **Comp. 83a,b** as compared with corresponding dialkoxyPPV homopolymers **Comp. 25a,b** (0.2 lm/W for ITO/**Comp. 83b**/Al). High ion-affinity of the oligoethyleneoxide pendant group allows to create light-emitting electrochemical cells (LEC) with efficiency of 0.5 lm/W (for ITO/**Comp. 83b**+LiOTf/Al).⁹⁰

Electroluminescence from related polymers **Comp. 84a,b** containing more sterically demanding 2,3-dibutoxyphenylene unit have been also studied. Both co-polymers are blue-green emitters (λ_{max} ~545 nm) with moderately high PL quantum yield in the solid state: 35% for **Comp. 84a** and 28% for **Comp. 84b**. In the same time, electroluminescence from **Comp. 84a** can be only observed with Ca electrode, whereas a single-layer device ITO/PEDOT/**Comp. 84b**/Al shows current efficiency of 0.72 cd/A and maximum luminance of 1,380 cd/m² (turn-on voltage 4 V).⁷⁹



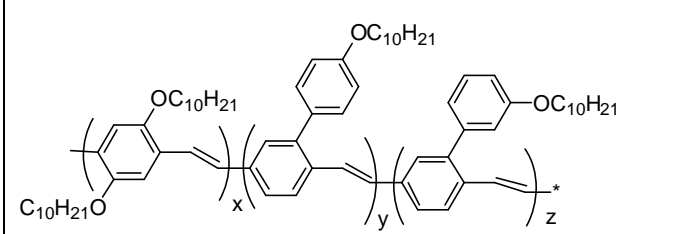
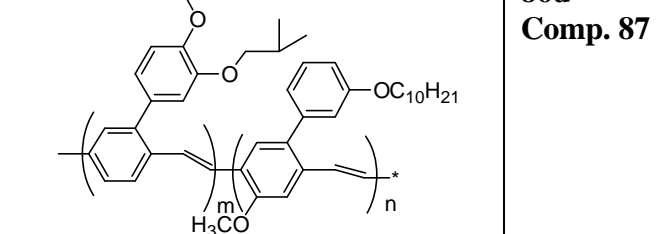
Synthesis of phenyl/alkoxy substituted PPV co-polymers was first reported by Spreitzer, Becker et al., who studied in details the dependence of the electroluminescence on the co-monomers ratio in **Comp. 86** (Scheme 15)⁷⁴ and other related phenyl-substituted PPV co-polymers.^{105,106,107} The polymerization was performed via Gilch route using different co-monomer feed ratios. All co-polymers showed high EL efficiency above 10 cd/A and low driving voltage (~3.5 V). In addition, very high emission brightness (10,000 cd/m²) was easily achieved by applying a very reasonable voltage of 6 to 8 V. The emission color of the phenyl-substituted PPV **Comp. 86a** is green (CIE: $x = 0.35$, $y = 0.61$), whereas increasing the ratio of dialkoxyphenylenevinylene results in gradual blue shift of the emission, through yellow (for **Comp. 86e**, CIE: $x = 0.49$, $y = 0.50$) to orange color (for **Comp. 86f**, CIE: $x = 0.60$, $y = 0.40$). Interestingly, the dialkoxyPPV homopolymer **Comp. 86f** itself revealed significantly lower EL efficiency of 2 cd/A but introducing the corresponded unit in the co-polymer in small amounts (2%, based on feed ratio) allows to increase the luminous efficiency from 10.6 lm/W (for **Comp. 86a**) to 16.1 lm/W (for **Comp. 86c**).



Scheme 15. Dependence of the electroluminescence of alkoxyphenyl-PPV co-polymers on the co-monomers ratio (PLED configuration ITO/PEDOT or PANI/polymer/Ca or Yb/Ag).

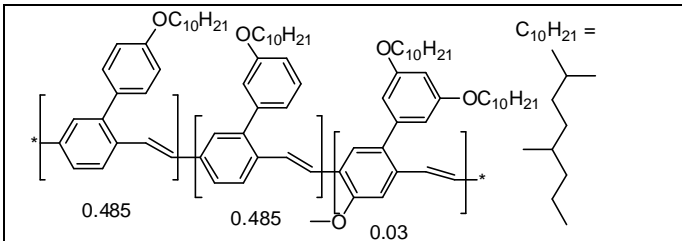
As we mentioned before, phenyl substituents in PPV increase the amount of TBB defects in Gilch synthesis, affecting the device stability. Becker et al. showed that introducing a second substituent (alkoxy-group) can significantly reduce the formation of TBB.¹⁰⁶ The TBB suppression was observed at increasing the feed ratio of alkoxy-phenyl substituted monomer. Scheme 16 shows the chemical structures of two greenish-yellow co-polymers and their EL performance along with their TBB defects. These two co-polymers have similar optical and electronic properties but their TBB contents are different. Hence, the device fabricated from low TBB-content co-polymer **Comp. 87** showed 30 times

longer lifetime than the device made from high TBB-content co-polymer even though their initial EL performance was nearly identical. Rather high life time of co-polymers of type **Comp. 87** made them attractive enough for industrial application in PLEDs, as pursuit by Philips and DuPont.¹³⁹

 <p style="text-align: center;">$x:y:z = 4:48:48$</p> <p>TBB: 6 % EL: 547 nm 10.5 cd/A 9.8 lm/W</p> <p style="text-align: center;">High TBB copolymer</p>	 <p style="text-align: center;">$m:n = 50 : 50$</p> <p>TBB: 2.5 % EL: 548 nm 9.3 cd/A 9.2 lm/W</p> <p style="text-align: center;">Low TBB copolymer</p>
Comp. 86d Comp. 87	

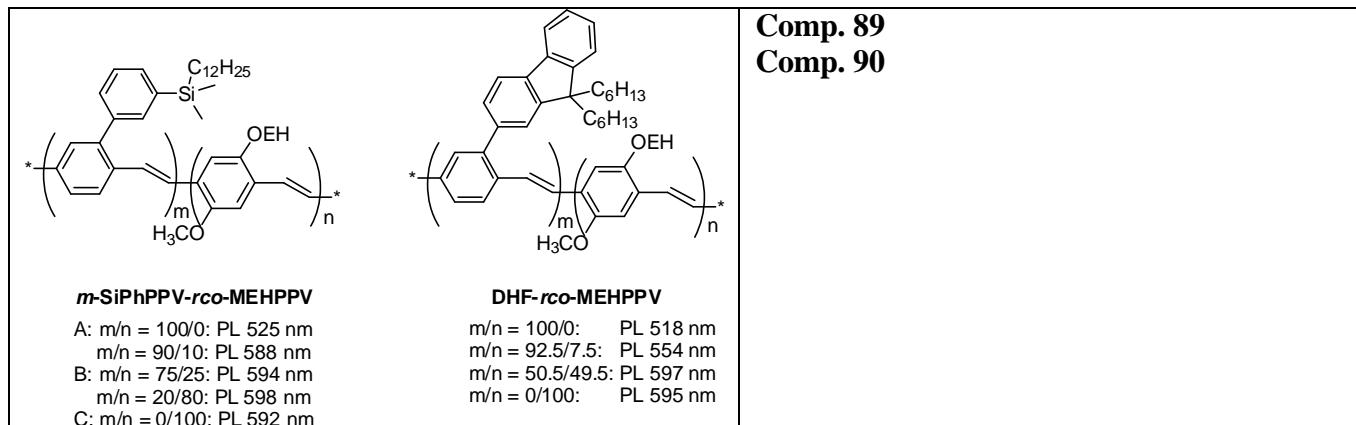
Scheme 16. The concentration of TBB defects and EL performance of two related phenyl-PPV co-polymers.

An extremely efficient PLED was fabricated with a similar phenyl-PPV co-polymer **Comp. 88** by the Cambridge group.¹⁴⁰ The PLED ITO/PEDOT/**Comp. 88**/Ca could be turned on at only 2.2 V and shows external Q.E. of amazing 6% [20 cd/A] (estimated internal Q.E. 15–20%, close to theoretical limit of 25%), which is still among the record values in the electrofluorescent PPV materials. Although this significant improvement was greatly due to sophisticated engineering of the anode/EL polymer interface (ITO was modified by multilayer deposition of PEDOT-based materials), the dialkoxyPPV homopolymer **Comp. 14** in same conditions showed essentially lower efficiency (1.8%, 2.6 cd/A).

	Comp. 88
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Scheme 17 illustrates some MEH-PPV random co-polymers with trialkylsilylphenyl (**Comp. 89**)¹¹³ and dihexylfluorene (**Comp. 90**)¹⁴¹ units, synthesized by Jin's group using Gilch polymerization method. The HOMO/LUMO energy levels and the emission color of these co-polymers can be finely tuned by adjusting the feed ratio of the co-monomers (Scheme 17, Figure 4). The authors found a dependence of the turn-on voltages on the gap between the HOMO level and the workfunction of ITO electrode, and suggested that holes are the major carriers in these materials. A high efficiency red-orange emitting ($\lambda_{\text{max}}^{\text{EL}} = 590 \text{ nm}$) PLED has been fabricated with co-polymer **Comp. 89** using low work function Al:Li alloy electrode.¹¹³ The device ITO/**Comp. 89**/Al:Li showed low turn-on voltage of 2.3 V, high maximum brightness over 19,000 cd/m² (at 12 V), high luminance efficiency 2.9 lm/W, and had half-lifetime 120 h at 1,000 cd/m², which significantly overrides the performance of similar devices prepared with both of corresponded homopolymers.

Likewise, co-polymers **Comp. 90** have higher EL efficiency than homopolymers DHF-PPV **Comp. 57** or MEH-PPV **Comp. 13**, due to more balanced charge injection/transport properties. Co-polymer **Comp. 90** with 7.5 wt% loading of dialkoxyphenylene co-monomer gave the highest quantum efficiency. The device in configuration of ITO/PEDOT/**Comp. 90**/Ca showed remarkably higher efficiency (2.4 cd/A) than those fabricated with other co-polymers in the series (0.65–1.0 cd/A).¹⁴¹



Scheme 17. Tuning the emission maxima in random phenyl-PPV co-polymers.

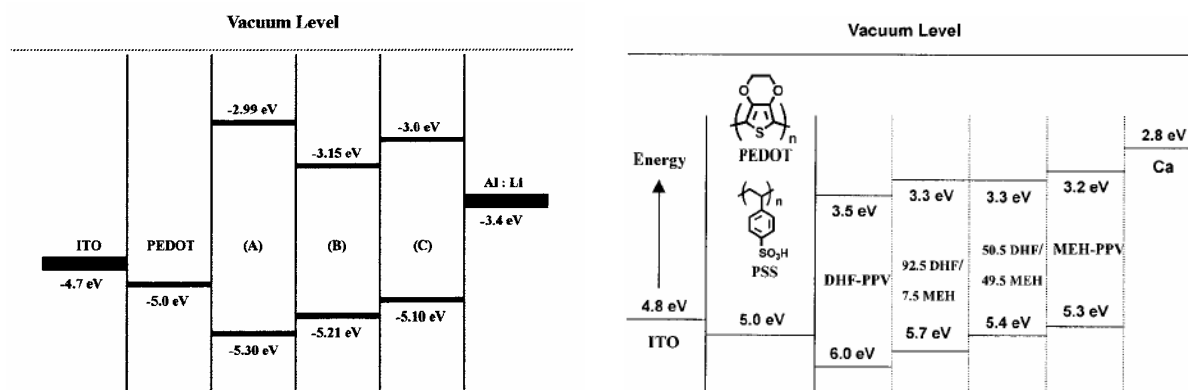
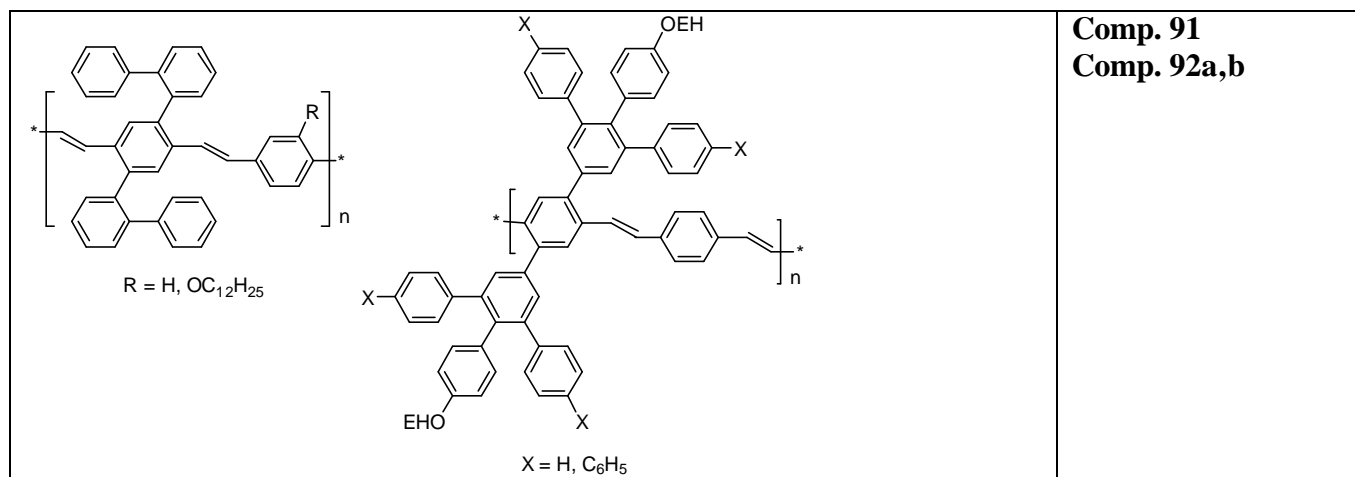


Figure 4. Energy diagrams of PLEDs based on polymers (left): **Comp. 89**(A,B,C); (right): **Comp. 90** with different feeding ratio (DHF stands for 9,9-dihexylfluorenyl). [From Ref. 113, © 2002 American Chemical Society and ref. 141, © 2002 American Chemical Society, respectively].

One of the problems in the design of organic (electro)luminescent materials is decrease of the quantum efficiency of fluorescence in the solid state due to formation of π -aggregates. Above we described several approaches to circumvent this problem by introducing bulky aromatic substituents into PPV backbone to hinder the intermolecular π -stacking. However, in homo-polymers, very bulky substituents slow down the polymerization reaction, resulting in low molecular weight products. The problem can be solved by introducing a second, less sterically demanding co-monomer unit. The polymer **Comp. 91**,¹⁴² synthesized by Peng et al. through Wittig-Horner reaction is a highly fluorescent material with PL quantum yield (in films) of 61–82 % (cf. 10 % for dioctyloxy-PPV). Unfortunately, no EL data was reported for these co-polymers.

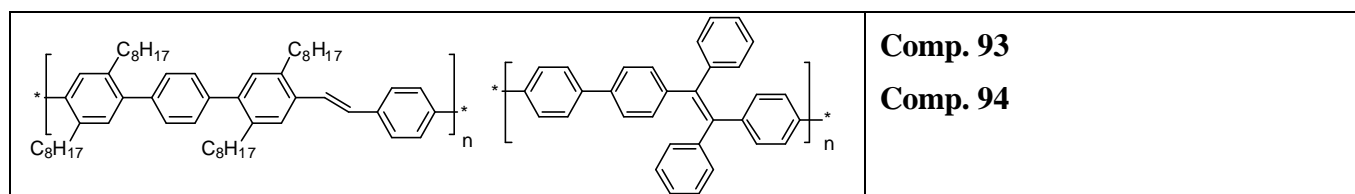
Even more bulky substituents were introduced in co-polymers **Comp. 92** synthesized by Heck coupling reaction.¹⁴³ These materials emit blue light with the maximum emission peak at 442 nm, which is among the shortest wavelength emission of the formally conjugated PPV. So short wavelength emission was attributed to the interruption the conjugation caused by oligophenylene substituents, although, as mentioned above, the aromatic substituents can adopt a nearly orthogonal dihedral angle in

respect to PPV chain minimizing the steric hindrances. Interestingly, in spite of these bulky substituents, the fluorescence spectra **Comp. 92** in films differs from those of solutions by an additional longer wavelength shoulder (at 512 nm), ascribed by authors to aggregates emission.

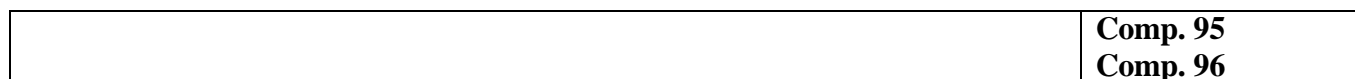


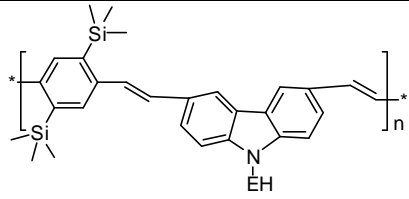
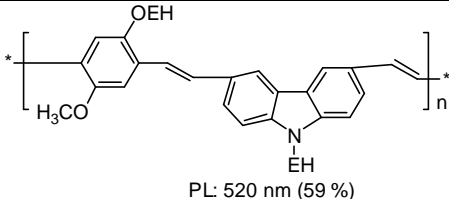
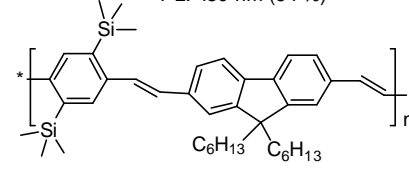
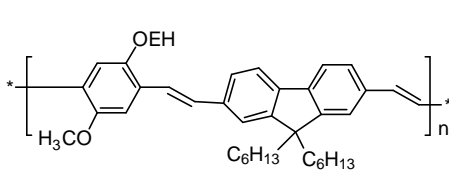
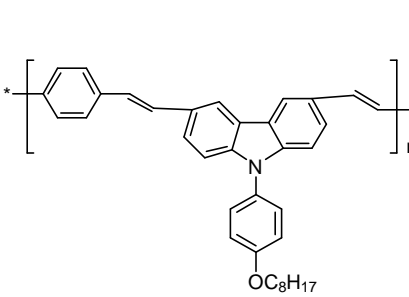
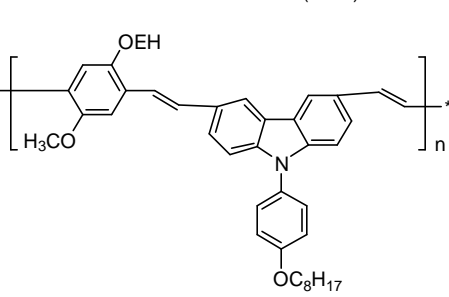
The properties of PPV polymers can be also tailored by introducing additional aromatic units in the PPV chain. In 1995, Hadziioannou et al. reported terphenylene-contained co-polymer **Comp. 93** synthesized by Heck's reaction.⁴⁶ Relatively poor conjugation brought by alkyl-substituted oligophenylene fragments (see Miscellaneous part of this chapter), results in blue shift of the emission wavelength (λ_{PL} = 440 nm in films; solution Φ_{PL} = 89–90%). A non-optimized single layer PLED (ITO/**Comp. 93**/Al) emitted blue light (λ_{EL} ~ 450 nm) with external Q.E. up to 0.03%.

Related copolymer **Comp. 94**, synthesized in 1980s by Feast et al, present a rare example of PPV containing phenyl substituents on the vinylene unit.¹⁴⁴ Apparently, the steric hindrances caused by phenyl substituents in **Comp. 94** are not dramatic, and the optical properties of **Comp. 94** are similar to those of other PPVs (green emission, λ_{PL} ~ λ_{EL} ~530 nm). The *internal* Q.E. of up to 1% were reported got multilayer **Comp. 94**-based PLEDs containing PPV **Comp. 1** and/or PVK as HTL.¹⁴⁵

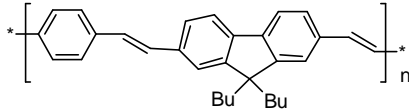
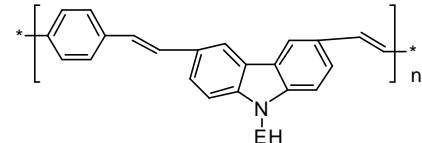
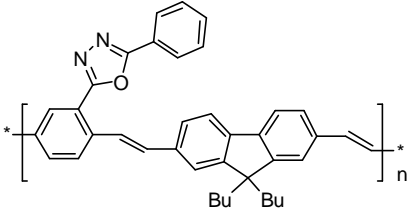
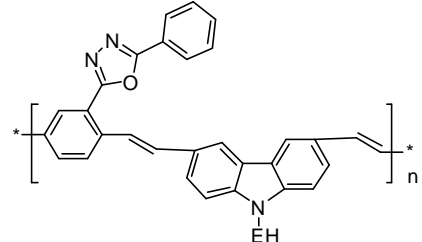


In the effort to make pure blue-emitting materials Shim et al. synthesized a series of PPV-based co-polymers containing carbazole (polymers **Comp. 95** and **Comp. 96**) and fluorene (polymers **Comp. 97** and **Comp. 98**) units, via Witting polycondensation.¹⁴⁶ Using the trimethylsilyl substituents instead of alkoxy groups eliminates the electron donor influence of the later and lead to chain distortion, which bathochromically shifts the emission (λ_{max} = 480 nm for **Comp. 95** and 495 nm for **Comp. 97**). Besides, a very high PL quantum efficiency was found for these polymers in the solid state (64 and 81%, respectively). Single layer PLEDs fabricated with **Comp. 95** and **Comp. 97** (ITO/polymer/Al) showed the EL efficiency 13 and 32 times higher than MEH-PPV, respectively (see also ref 147 for synthesis and PLED studies of polymers **Comp. 99** and **Comp. 100**).

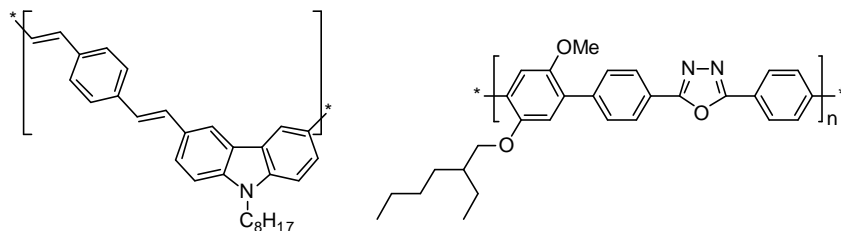


 <p>PL: 480 nm (64 %)</p>	 <p>PL: 520 nm (59 %)</p>	Comp. 97 Comp. 98 Comp. 99 Comp. 100
 <p>PL: 495 nm (81 %)</p>	 <p>PL: 540 nm (26 %)</p>	
 <p>UV: 388 nm, PL: 576 nm (THF), HOMO: -5.20 eV, LUMO: -2.47 eV</p>	 <p>UV: 415 nm, PL: 503 nm (THF), HOMO: -5.16 eV, LUMO: -2.60 eV</p>	

Similar PPV-based copolymers with carbazole and fluorene units in the backbone **Comp. 101** and **Comp. 102** (and also similar copolymers with oxadiazole substituents **Comp. 103** and **Comp. 104**) have been synthesized by Ree et al.¹⁴⁸ Much lower PL efficiency in films was found in this case for carbazole-containing polymers **Comp. 102** and **Comp. 104** (1–4%) as compared to materials prepared by Shim (**Comp. 95** and **Comp. 96**, 59–64%).

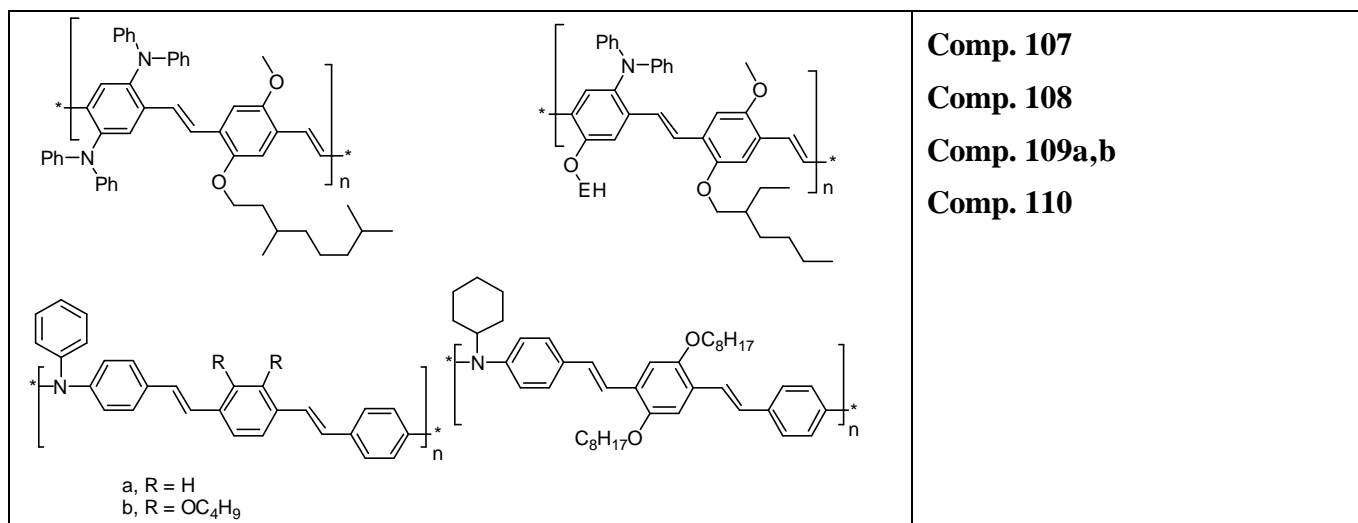
 <p>UV: 370 nm, PL: 473 nm (24 %)</p>	 <p>UV: 360 nm, PL: 500 nm (1 %)</p>	Comp. 101 Comp. 102 Comp. 103 Comp. 104
 <p>UV: 368 nm, PL: 473 nm (14 %)</p>	 <p>UV: 376 nm, PL: 521 nm (4 %)</p>	

Blends of yellowish-green-light emissive carbazole-containing PPV-based co-polymer **Comp. 105** ($\lambda_{PL} = 490, 520\text{sh nm}$, $\lambda_{EL} = 533\text{ nm}$) with blue-emissive oxadiazole-PPP co-polymer **Comp. 106** ($\lambda_{EL} = 426\text{ nm}$) allowed to tune the emission of PLEDs (ITO/polymer blend/Al) from $\lambda_{EL} = 533\text{ nm}$ to $\lambda_{EL} = 451\text{ nm}$ although the device turn-on voltage was essentially higher for the blends with increased content of **Comp. 106**.¹⁴⁹

**Comp. 105****Comp. 106**

The diphenylamino-substituted PPV **Comp. 107** with solubilizing alkoxy group was synthesized by Zheng et al. via Wittig-Horner reaction.¹⁵⁰ Its photoluminescence (555 nm) is very similar to that of diamino-PPV **Comp. 64** and dialkoxy-PPV **Comp. 14** homopolymers. The PL quantum yield is rather high in solution (80%), but it drops to only 8% in films. Consequently, only moderate efficiency of 0.6 cd/A was obtained with this material (device ITO/PEDOT/**Comp. 107**/Mg/Al).¹⁵⁰ Almost simultaneously, Kido et al. reported a similar diphenylamino-substituted PPV co-polymer **Comp. 108**, which affords very efficient PLEDs.¹⁵¹ The device ITO/PEDOT/**Comp. 108**/Ca/Al showed low turn-on voltage (3 V), high maximal brightness (29,500 cd/m²) and power efficiency of 1.1 lm/W, which can be further improved to 3.0 lm/W if cesium is used as a cathode.

The amino group has also been introduced in the PPV backbone. Co-polymers **Comp. 109**, **Comp. 110** (and some derivatives incorporating additional phenylene, naphthalene or anthracene units in the main chain¹⁵²) have been synthesized by Wittig-Horner reaction as green-emitting materials ($\lambda_{PL} \sim 530$ nm) with moderate PL quantum yield (10–15% in films).¹³⁸ Preliminary device testing demonstrated improved hole-transport properties in these materials [manifested as a decrease of the turn-on voltage to 2.4–2.8 V, for ITO/PEDOT/**Comp. 109b**/Ca(Al)], although the efficiency of the unoptimized device was very low (0.001 cd/A). Even lower turn-on voltage of 1.5 V was reported for PLED ITO/ **Comp. 109a**/Al.¹⁵²

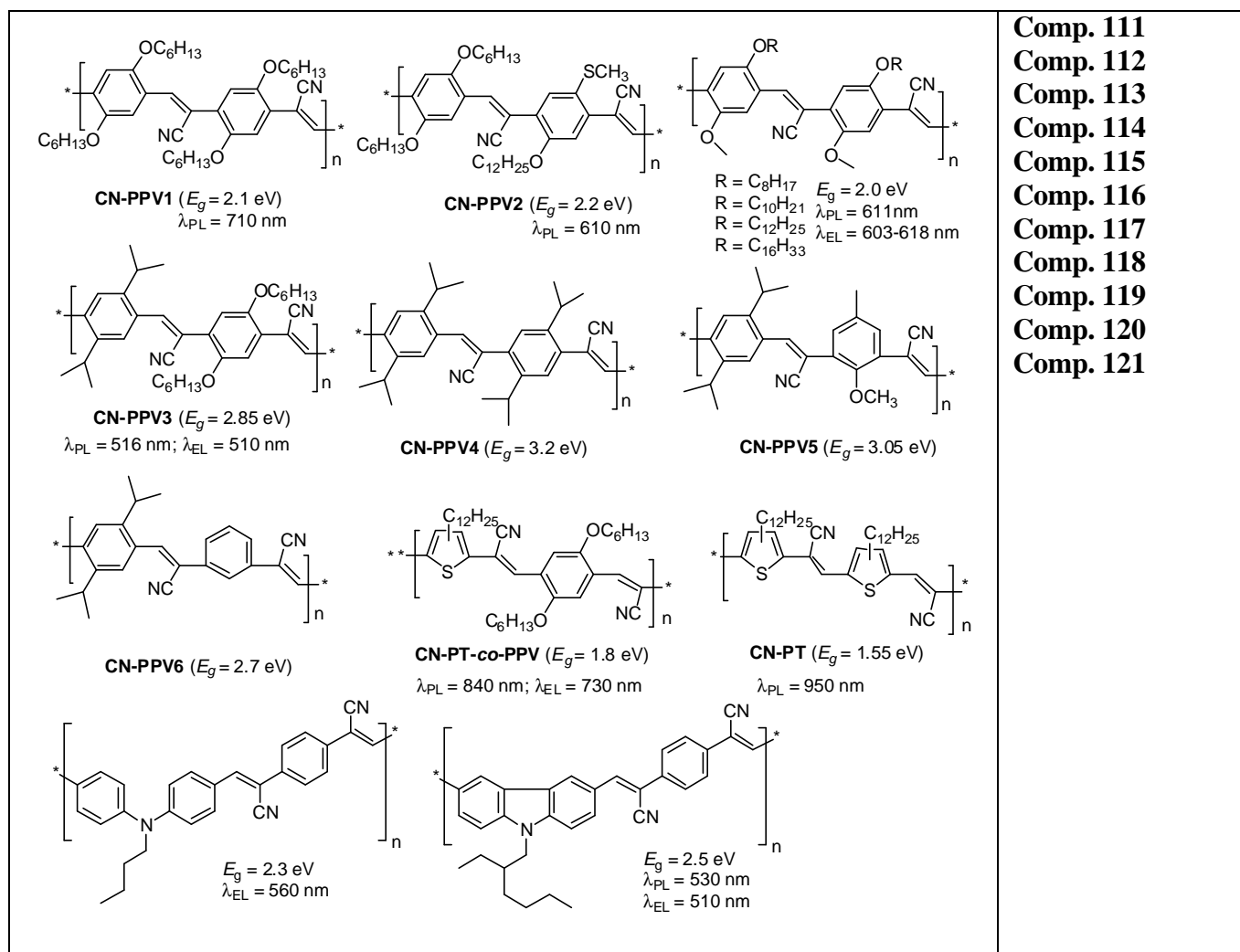
**Comp. 107****Comp. 108****Comp. 109a,b****Comp. 110**

1.3.2. PPV co-polymers with electron-withdrawing substituents.

The first PPV bearing a cyano group attached to vinylene fragment was synthesized as early as in 1960 as unprocessable and insoluble material, which could not be used in PLEDs.⁴³ Electron acceptor cyano substituents lower the HOMO and LUMO levels of the polymer by ca. 0.6 eV and 0.9 eV, respectively. In 1993 Cambridge group at UK reported the first soluble phenylene cyanovinylene (CN-PPV) co-polymers (**Comp. 111**, **Comp. 112**) synthesized by Knoevenagel condensation

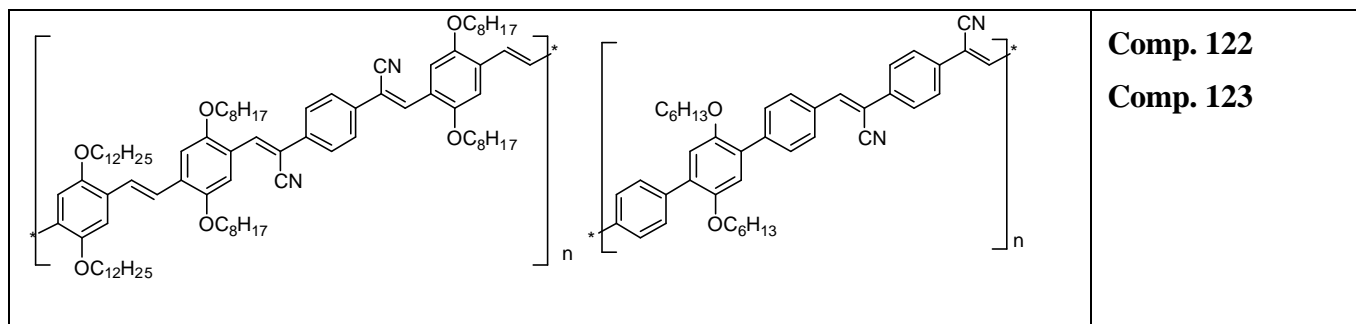
polymerization.¹⁵³, although the presence of two electron-donor alkoxy substituents significantly reduces the electron-accepting effect brought by the cyano group. Nevertheless, as compared to most widely used dialkoxy-PPVs, the electron injection (and transport) in **Comp. 111** and **Comp. 112** is facilitated, allowing to use less reactive aluminum electrode instead of calcium in PLEDs (both give the same EL quantum efficiency). On the other hand, cyano group reduces the hole-transporting properties of the diode, which had to be adjusted by introducing a second layer of a hole-transporting material (unsubstituted PPV **Comp. 1**). The double layer PLEDs ITO/PPV **Comp. 1**/CN-PPV/Al emitted red (for **Comp. 111**) or yellow-orange (for **Comp. 112**) light with rather high (for the time) *internal* quantum efficiencies of 4% and 2%, respectively. Following this initial report, a series of other CN-PPV derivatives **Comp. 113**¹⁵⁴ and **Comp. 114–Comp. 117**⁴⁴ and thiophene analogues **Comp. 118** and **Comp. 119**⁴⁴ have been synthesized by Knoevenagel method. This reaction appears to be a convenient way to a number of different substituted PPVs, with finely tuned band gap and emission wavelength (Scheme 18). The PLEDs with blue (**Comp. 114–Comp. 117**), red (**Comp. 111, Comp. 112**) and near-IR (**Comp. 118, Comp. 119**) emission have been fabricated with these polymers. A remarkably high (as for PPV) band gaps of over ~3 eV was achieved for bis(*i*-propyl)-substituted co-polymers **Comp. 114–Comp. 117**, probably due to backbone distortion.

Knoevenagel coupling has been also used to synthesize the CN-PPV co-polymers with diphenylamino donor unit (**Comp. 120**).¹⁵⁵ In spite of short solubilizing group (butyl), **Comp. 120** is a very soluble polymer, which is due to rather low molecular weight $M_n = 5700$. A simple PLED ITO/**Comp. 120**/Al can be turned on at 4.5 V emitting at $\lambda_{\text{max}}^{\text{EL}} = 560$ nm, but the efficiency of the device was not reported. A related donor-acceptor CN-PPV co-polymer **Comp. 121** was synthesized with essentially higher molecular weight $M_n = 37000$.¹⁵⁶ The PLED device thereof was fabricated as ITO/**Comp. 121**/Al, but its efficiency and the brightness was not reported in the paper.

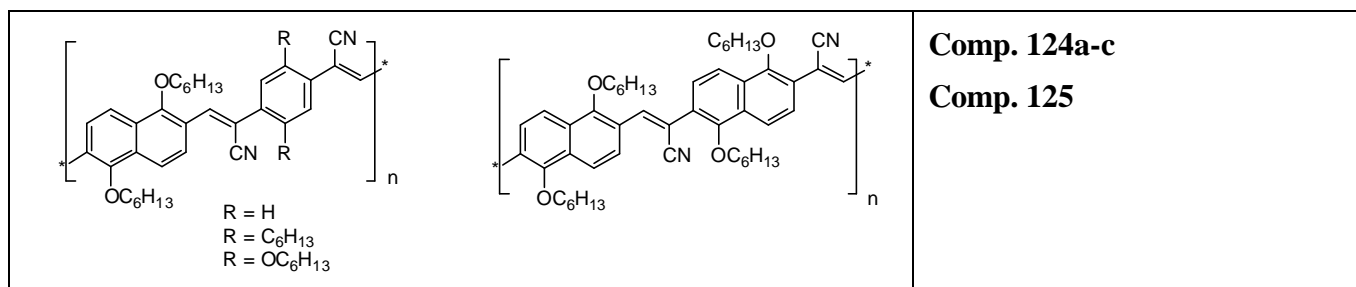


Scheme 18. Band-gap and emission tuning in cyano-substituted PPVs.

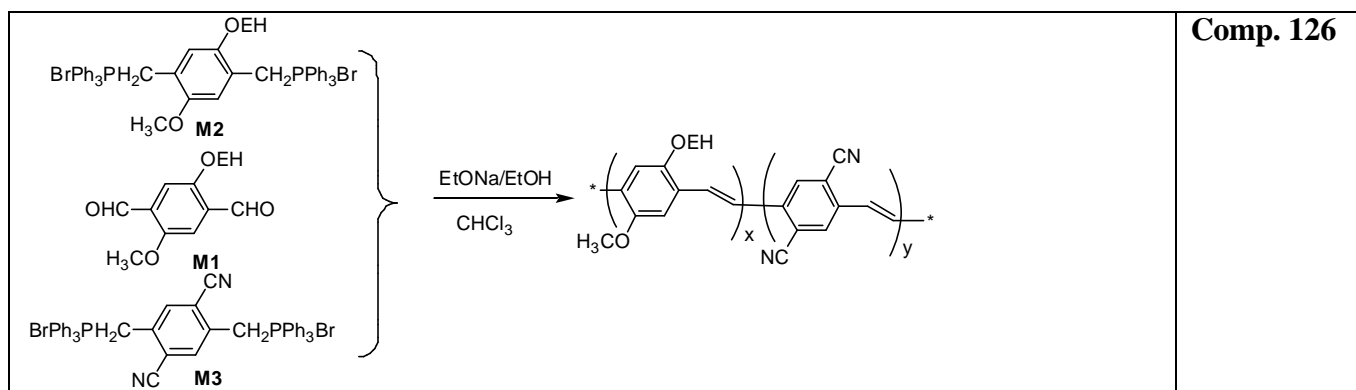
Heck and Suzuki coupling polymerization have been used to synthesize CN-PPV co-polymers **Comp. 122**¹⁵⁷ and **Comp. 123**,¹⁵⁸ respectively. As expected, decreasing the number of cyano-groups, as compared to CN-PPV **Comp. 111** destabilizes the LUMO orbital increasing the band-gap, which is the same for both compounds [**Comp. 122**: $E_g(\text{optical}) = 2.37$ eV; **Comp. 123**: $E_g(\text{optical}) = 2.38$ eV, $E_g(\text{electrochemical}) = 2.37$ eV]. The solid-state emission maxima are also identical (590 nm). The external Q.E. (0.025 %) demonstrated by **Comp. 122** in a simple device ITO/polymer/Al can be increased to 0.062% by applying a second layer of PPV **Comp. 1** between the ITO and light-emitting layers. For the polymer **Comp. 123**, significantly lower EL efficiency was obtained, in spite of more optimized device structure: the external Q.E. of ITO/copper phthalocyanine HTL/**Comp. 123**/Ca/Ag was only 0.011% (and the maximal brightness of 213 cd/m²).



Hanack et al. reported related cyano-substituted naphthalene vinylene derivatives **Comp. 124**, **Comp. 125**.¹⁵⁹ Interestingly, replacing the phenylene unit in CN-PPV **Comp. 111** with naphthalene in polymers **Comp. 124**, **Comp. 125** results in significant blue shift of the emission maxima from 710 nm to 595 nm (for **Comp. 124a**) and 500 nm (for **Comp. 125**). However, the efficiency, tested for double-layer device ITO/**Comp. 1**/**Comp. 125**/Mg:Al(3:97), was rather low (external Q.E. 0.017%).

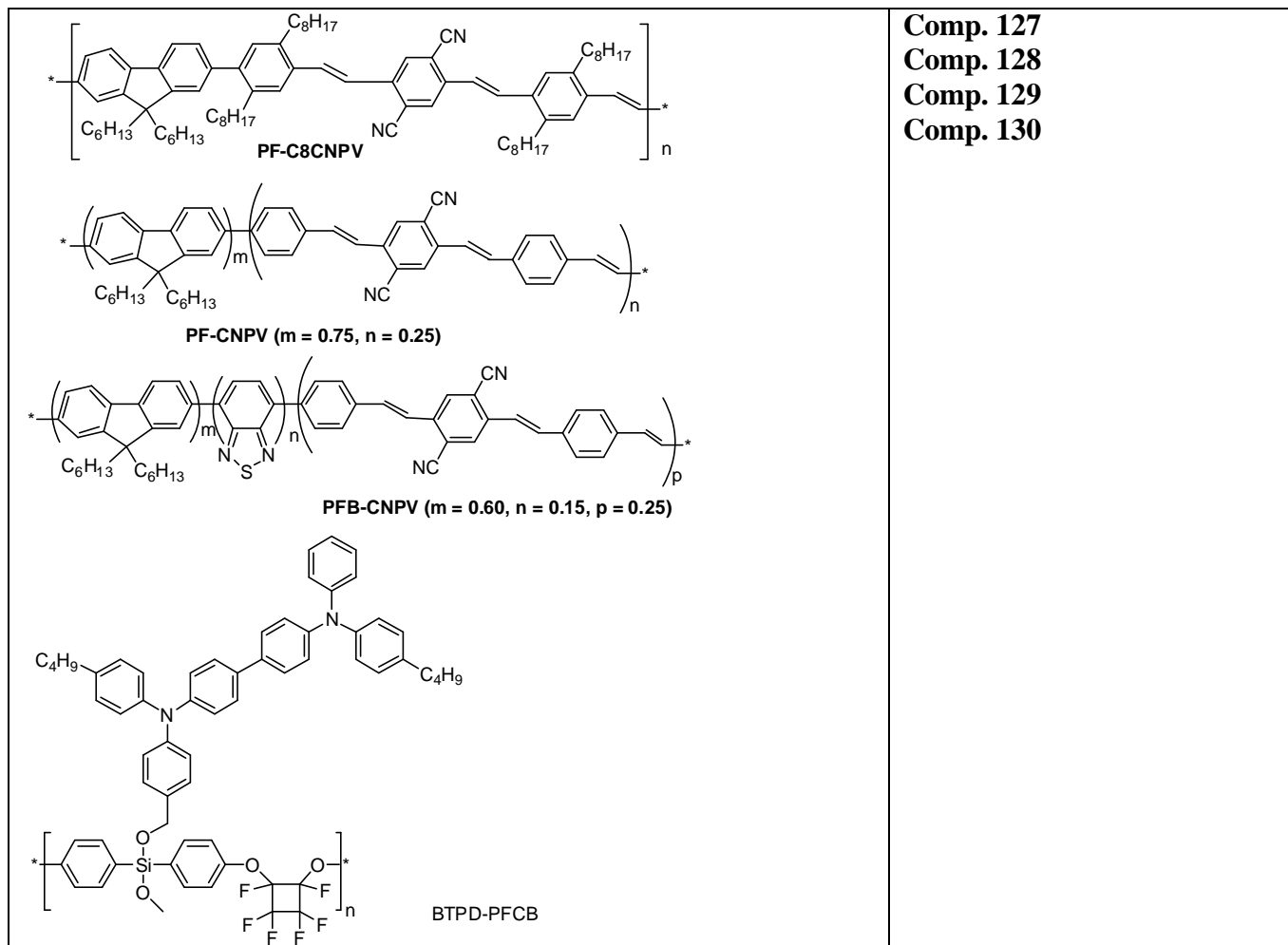


Following the CN-PPV series, another electron deficient co-polymer **Comp. 126**, in which the cyano groups are attached to the phenylene units has been synthesized by Huang et al. (Scheme 19).^{160,161} Due to more efficient conjugation of two cyano groups within the phenylene unit, this polymer possesses a stronger electron affinity than **Comp. 111–Comp. 119**. The co-polymers **Comp. 126** with different ratio of dicyanophenylene vinylene and dialkoxyphenylene vinylene units have been synthesized. Changing the feed ratio of co-monomers M2 and M3, the HOMO/LUMO energy levels can be finely adjusted, and the electron affinity of the co-polymer having a 1:1 ratio of M2 to M3 is higher than that of MEH-PPV by over 0.8 eV (cf. 0.4 eV for same ratio CN-PPV co-polymer). A single layer PLED (ITO/**Comp. 126** (x=y)/Al) emits pure red light ($\lambda_{PL} = 610$ nm), but no characteristics of the device except a low turn-on voltage (4–6 V) was reported.¹⁶¹

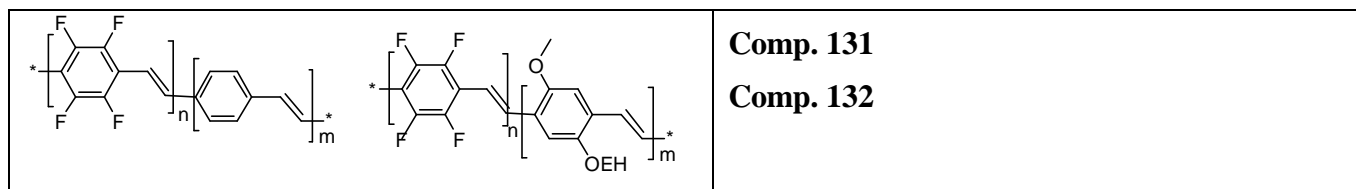


Scheme 19. Synthesis of dicyanophenylenevinylene co-polymers by Wittig condensation.

The 2,5-dicyanophenylene unit has also been used by Jen et al. in synthesis of a series of polyfluorene – PPV co-polymers **Comp. 127–Comp. 129** through Suzuki-coupling reactions.¹⁶² An important, although somewhat discouraging point discovered within this series was an observation of inverse correlation between the electron affinity and the PL quantum yield (PL quantum yield was 17% for **Comp. 127**, 15% for **Comp. 128** and 10% for **Comp. 129**), i.e. strong electron acceptor moieties tend to quench the photoluminescence. Nevertheless, the polymer **Comp. 127** showed a quite respectable performance in the double layer device containing a hole-transport layer (HTL) of BTPD-PFCB polymer (**Comp. 130**): ITO/HTL/**Comp. 127**/Ca PLED had very low switching voltage (2.6 V), high external Q.E. (0.88 %) and brightness of 4,730 cd/m² achieved at 1.62 A/cm².



Neumann et al. synthesized tetrafluorinated PPV co-polymer **Comp. 131** and studied its light-emitting properties.¹⁶³ However, this material was quite unsuccessful for LED applications: increasing the amount of fluorinated co-monomer resulted in dramatic decrease of the PL quantum yield, and the turn-on voltage of the devices was above 30 V (which could only be realized in *ac* mode due to device shortening). The quenching was less pronounced for an analogous co-polymer with MEH-PPV (**Comp. 132**), which showed the EL efficiency up to 0.08 cd/A (in ITO/PEDOT/**Comp. 132**/Ca diode).¹⁶⁴

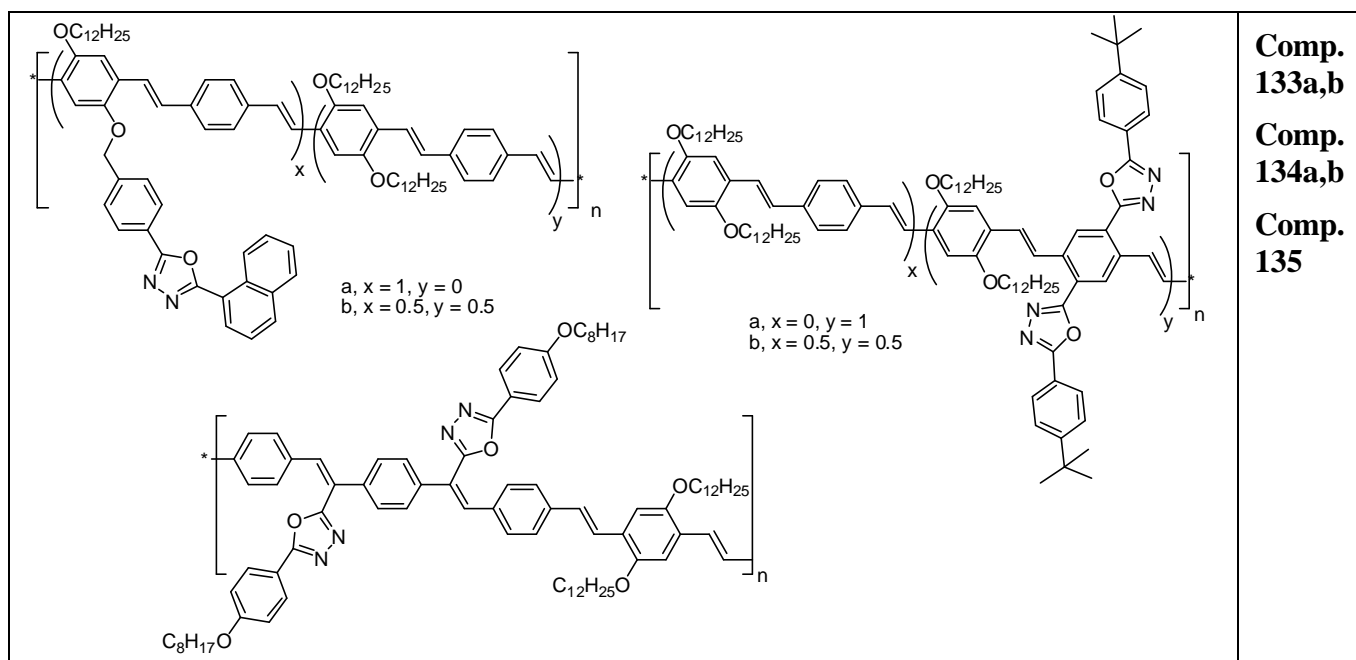


As we already mentioned, electron-transporting properties of PPV polymers can be adjusted by introducing oxadiazole moiety in the polymer structure. A variety of PPV co-polymers containing oxadiazole unit as a pendant group have been synthesized to date. Among the first, in 1998 Bao et al. reported co-polymers **Comp. 133** containing phenyl(naphthyl)oxadiazole moiety separated from the PPV backbone by an oxymethylene bridge.¹³⁵ The PL emission of **Comp. 133** ($\lambda_{\text{PL}} = 580 \text{ nm}$) is almost unperturbed by the presence of the oxadiazole moiety, but the EL efficiency measured with Al and Ca cathodes suggest the electron transport has been significantly improved in these materials, as compared to dialkoxy-PPVs (e.g., $\Phi_{\text{EL}}^{\text{ex}} = 0.002\%$ for a related device ITO/**Comp. 81c**/Al).¹³⁵ In fact, the external Q.E. was higher with Al cathode (0.02%) than with Ca (0.015%), and, in contrast to dialkoxy-PPV, adding PBD as an additional electron-transport material only decreases the device efficiency (0.013%).

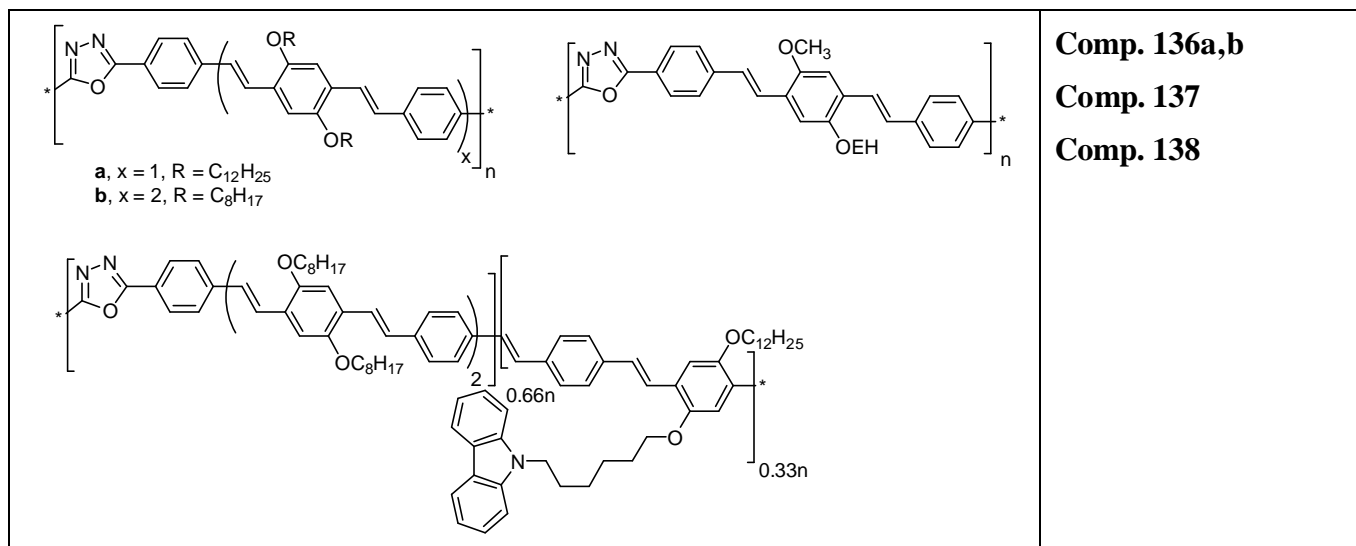
A year later, Peng et al. reported PPV **Comp. 134** containing two oxadiazole substituents attached immediately to the polymer backbone (to the phenylene unit).¹³⁶ Comparing to the previous oxadiazole-PPV, the external Q.E. in **Comp. 134** was further improved to 0.045% (ITO/**Comp. 134b**/Al) and the maximal brightness of $1,160 \text{ cd/m}^2$ was reported.

Lee et al. reported an efficient light-emitting polymer, containing the oxadiazole groups, attached to the vinylene units of PPV.¹⁶⁵ Polymer **Comp. 135** was synthesized by Heck polymerization of dialkoxydivinylbenzene with oxadiazole-contained aromatic dibromide. The PL efficiency **Comp. 135** ($\lambda_{\text{max}} = 560 \text{ nm}$) in films was 6.5 higher than that of MEH-PPV **Comp. 13**, and the energy levels were more favorable for electron transport: **Comp. 135**, HOMO = -5.30 eV , LUMO = -3.10 eV ; cf. MEH-PPV **Comp. 13**, HOMO = -4.98 eV , LUMO = -2.89 eV (all determined electrochemically). The PLED device ITO/PEDOT/**Comp. 135**/Al showed relatively high external Q.E. of 0.34%, with maximum luminance of $1,450 \text{ cd/m}^2$ (at 13 V). Again, changing the Al electrode for Ca resulted in only a small increase of the Q.E. (0.43 %), suggesting that the charge-transport properties **Comp. 135** are relatively well-balanced.

Recently Jenekhe et al. reported on four PPV derivatives containing one or two quinoxaline moieties per repeat unit, either in the main chain or as a pendant groups.¹⁶⁶



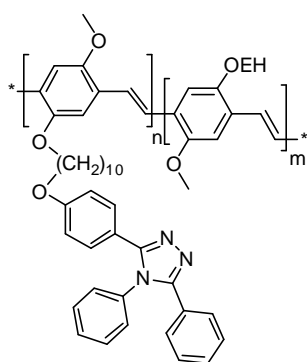
Several groups introduced oxadiazole moiety as a part of the PPV backbone (polymers **Comp. 136a**,¹⁶⁷ **Comp. 136b**,¹⁶⁸ **Comp. 137**,¹⁶⁹ **Comp. 138**¹⁶⁷). Not unexpected, the oxadiazole moiety lowers the LUMO energy of these polymers (as demonstrated by CV measurements). The decreased electron injection barrier is manifested by lowered turn-on voltage (6 V for ITO/**Comp. 136b**/Al).¹⁶⁸ However, relatively low efficiency (0.15% for **Comp. 136b**¹⁶⁸) was reported for these co-polymers.



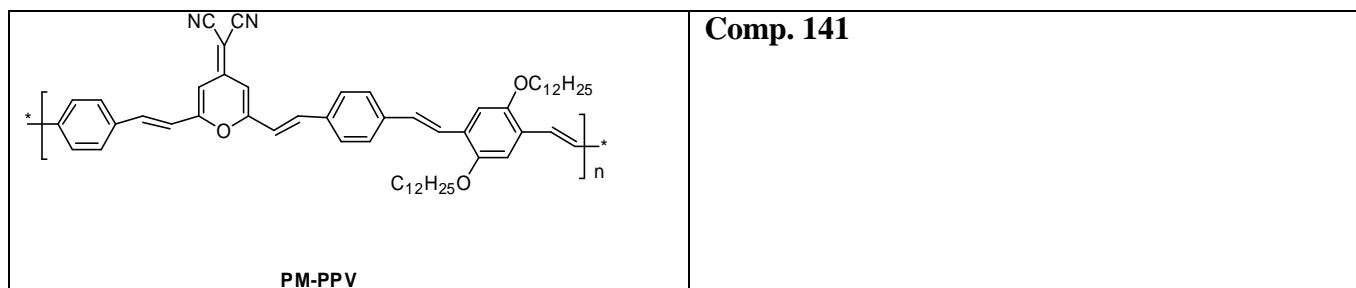
Burn et al. synthesized co-polymer **Comp. 139** containing a similar electron-deficient moiety (triazole) incorporated in the PPV backbone. They have reported an efficient blue emission from this polymer [$\lambda_{PL} = 466$ nm (solution), 486 nm (film), $\Phi_{PL} = 33$ % (film)] although the efficiency of the PLED fabricated as ITO/PPV/**Comp. 139**/Al was not very high (the external Q.E. reached 0.08% at a luminance of 250 cd/m²).¹⁷⁰



Most recently, Chen et al. reported co-polymer **Comp. 140** incorporating a triphenyltriazole moiety as a pendant group.¹⁷¹ Increasing the proportion of electron-deficient triazole moieties (n:m) improves the electron-transport properties of the material, as demonstrated by increase of the EL efficiency from 0.2 cd/A (for n:m = 0:1, MEH-PPV) to 3.1 cd/A (for n:m = 4:1), for the ITO/PEDOT/polymer/Al device configuration. In the same time, for the devices ITO/PEDOT/polymer/Ca, where the electron transport is already improved by using low work-function electrode, the device efficiency stays at the level of 1–2 cd/A for all range of polymer composition (n:m). Very high brightness of 17,000–19,000 cd/m² was observed for these devices.

**Comp. 140**

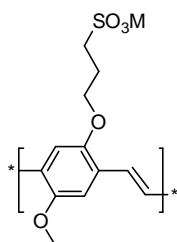
By analogy with Kodak's low molecular dyes, Kim and Lee. introduced an electron acceptor dicyanomethylenepyran moiety into the PPV co-polymer chain.¹⁷² The PPV co-polymer **Comp. 141**, synthesized by Heck coupling polymerization revealed strong pure red-color emission (λ_{max} : 646 nm; CIE: $x = 0.67$, $y = 0.33$). The downshifted orbital levels of **Comp. 141** (HOMO: –5.44 eV, LUMO: –3.48 eV) compared with MEH-PPV **Comp. 13** (HOMO: –4.98 eV, LUMO: –2.89 eV) result in more balanced holes/electrons injection, and the single layer PLED fabricated as ITO/**Comp. 141**/Al showed eight times higher EL efficiency than the PLED fabricated with MEH-PPV.



Porphyrine chromophore unit have been also introduced in the PPV backbone, but the PL quantum yield of such materials decreased rapidly with increasing the ratio of the porphyrine units, and no electroluminescent devices thereof have been reported.^{173,174}

1.4. PPV polyelectrolytes.

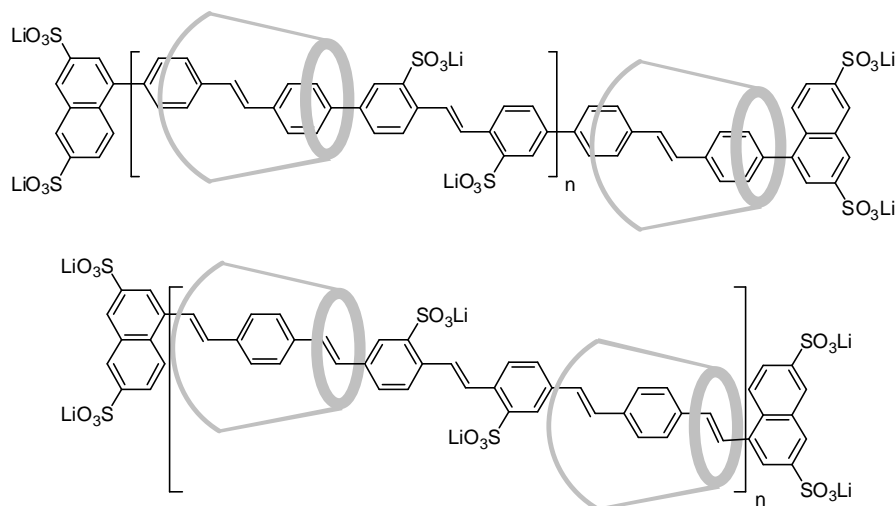
For developing a cost-effective environment-friendly fabrication process, and also for making a link for a possible application in biological systems, it is desirable to have water-processable light-emitting polymers. In this line, Wudl et al. synthesized water soluble PPV **Comp. 142** containing ionic sulfoxy groups, isolated from the PPV backbone by an alkyl chain.¹⁷⁵ This material appeared to be highly fluorescent with λ_{PL} in the range of 550–600 nm, depending on the solid state structure (engineered by self-assembly of the anionic PPV **Comp. 142** multilayers separated by counter-ion layers).¹⁷⁶ Taking advantage of good compatibility of polymer **Comp. 142** with aqueous media and the known quenching amplification in conjugated polymers, highly efficient fluorescent biological sensors have been designed with this material.¹⁷⁷ Unfortunately, no PLED or, which would be more interesting, LEC devices with **Comp. 142** have yet been reported.



M = H, Na, NH₄

Comp. 142

Anderson et al. reported water soluble polyrotaxanes **Comp. 143**, **Comp. 144** containing sulfonated PPV chains surrounded by mechanically bound α - and β -cyclodextrin macrocycles.^{178,179,180} The cyclodextrin rings play a role of a “wire insulator”, preventing the aggregation and interchain quenching. The effect was demonstrated by AFM, which showed individual polymer chains for cyclodextrin-encapsulated polymer, but not for the non-complexed material. The photoluminescence (for **Comp. 144**¹⁸⁰) and electroluminescence efficiency (for **Comp. 143**¹⁷⁸) for the complexed material was ~3–4 times higher than those for non-complexed polymer. However, the absolute value of external Q.E. (~0.025%) was very low as for practical application, which was not only due to unoptimized device structure (ITO/**Comp. 143**/Ca), but also due to generally low PL quantum yield of the polymer containing a sulfoxy group directly attached to the backbone.



Comp. 143

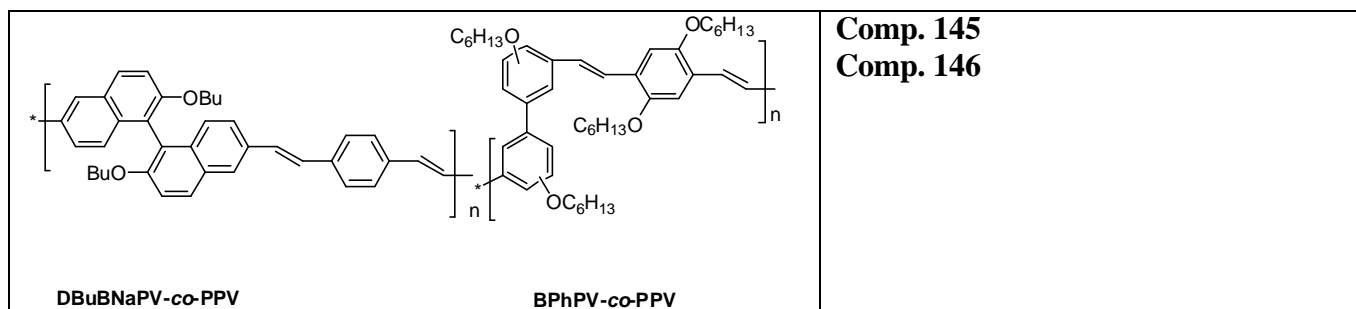
Comp. 144

1.5. Controlling the conjugation in PPV polymers

So far we have demonstrated that PPV derivatives are among the most popular materials for PLED and different color emission can be achieved by substitution but, with few exceptions,^{104,143} blue color is not available for fully conjugated PPV. Furthermore, rigid rod structure of a highly conjugated chain results in high crystallinity of many PPV materials, which is held responsible for decrease of the PL efficiency in the solid state and the pin-hole defects in thin films. The following two sections present current approaches to this problem via control of the conjugation length in PPV materials.

1.5.1. Formally conjugated systems with twists, meta-links and *sp*-hybridized atoms in the mainchain.

Intramolecular π -stacking can be effectively prevented by introducing a twist structure in the main backbone of PPV, which also essentially reduce the conjugation along the chain and is expected to result in hypsochromic shift of the emission. This kind of twist was achieved by co-polymerization with binaphthyl or biphenyl units (**Comp. 145**¹⁸¹ and **Comp. 146**¹⁸²). Twisted binaphthyl co-polymer **Comp. 145** based PLED (fabricated with ITO and Al electrodes) exhibited blue-green light emission with external Q.E. of 0.1 % and a relatively low driving voltage of 6 V. Similar moderate results were found for biphenyl co-polymer **Comp. 146**. The PLEDs fabricated as ITO/PEDOT/**Comp. 146**/Ca/Al emit green-blue light ($\lambda_{\text{max}}^{\text{EL}}$ 485–510 nm, depending on substituents pattern) with external Q.E. 0.17%. The authors explained the lower Q.E. of the co-polymers by interruption of the conjugation by the twisted units, which increases a nonradiative relaxation. Importantly, in both cases, due to interrupted conjugation, the emission band undergoes a significant hypsochromic shift.



In fact, blue emitting PPV material are the subject of significant research interest, as blue electroluminescence is the key for creating full color EL displays. However, this is generally unavailable for conjugated PPVs due to relatively low band gap. Consequently, several strategies to decrease the effective conjugation length have been studied in search of blue-emitting PPVs. This can be achieved by either introducing a non-conjugated blocks or sp^3 “defects” into PPV chain (see conjugated/nonconjugated co-polymers below) or changing the attachment mode of the phenylene unit in the chain. The synthesis of substituted poly(*m*-phenylene vinylene) and poly(*o*-phenylene vinylene) homopolymers have been reported 1993 by Leung and Chik, although with no connection to controlling the luminescent properties of the polymer.⁹² In 1999 Shim et al. synthesized and studied a series of dialkoxy- and bis(trimethylsilyl) substituted PPV co-polymers with *o*-, *m*- and *p*-phenylene structure (**Comp. 147–Comp. 152**).¹⁸³ The meta-linking of the phenylene unit does not allow for direct conjugation, resulting in hypsochromic shift of both absorption and emission bands. The ortho-linking, although formally conjugated, brings essential steric hindrances which distort the polymer chain and

decrease the effective conjugation length (although not as strong as *m*-linking). Combining these structural changes with substituents variations, fine tuning of the electroluminescence wavelength was achieved (Figure 5).

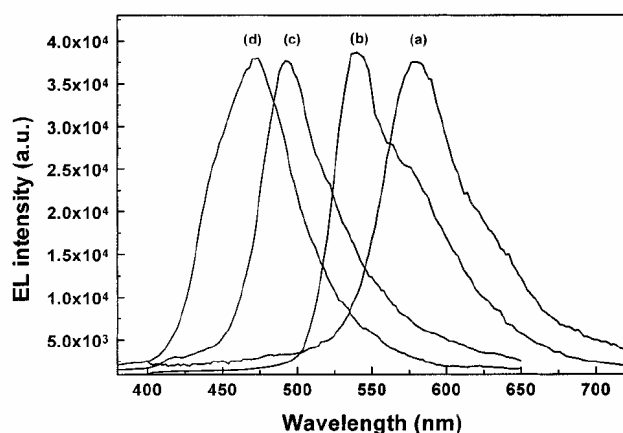
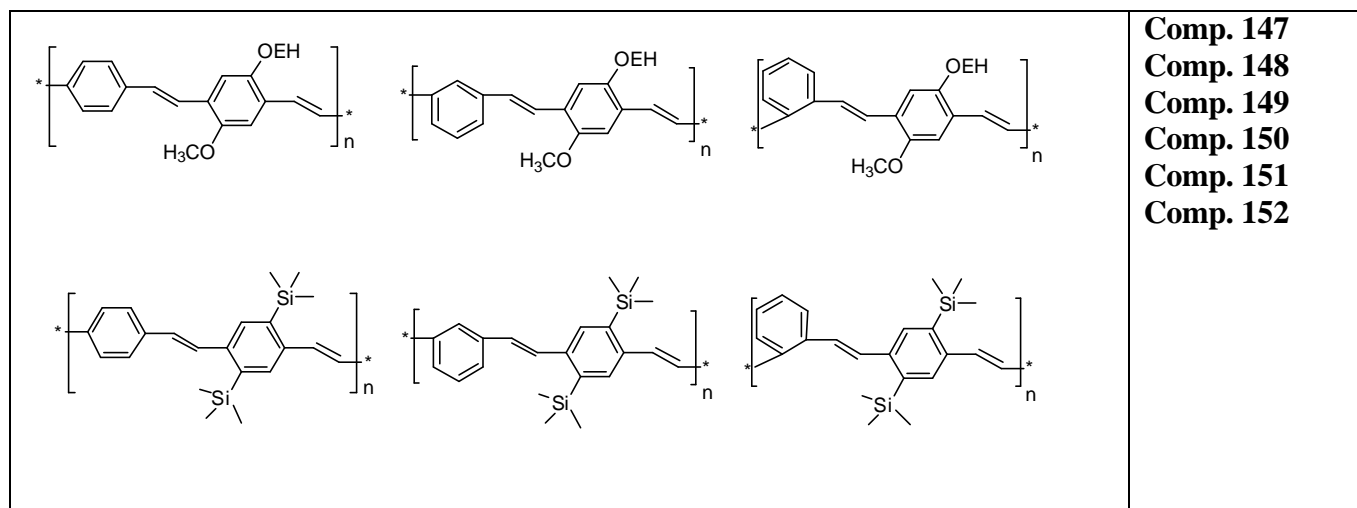


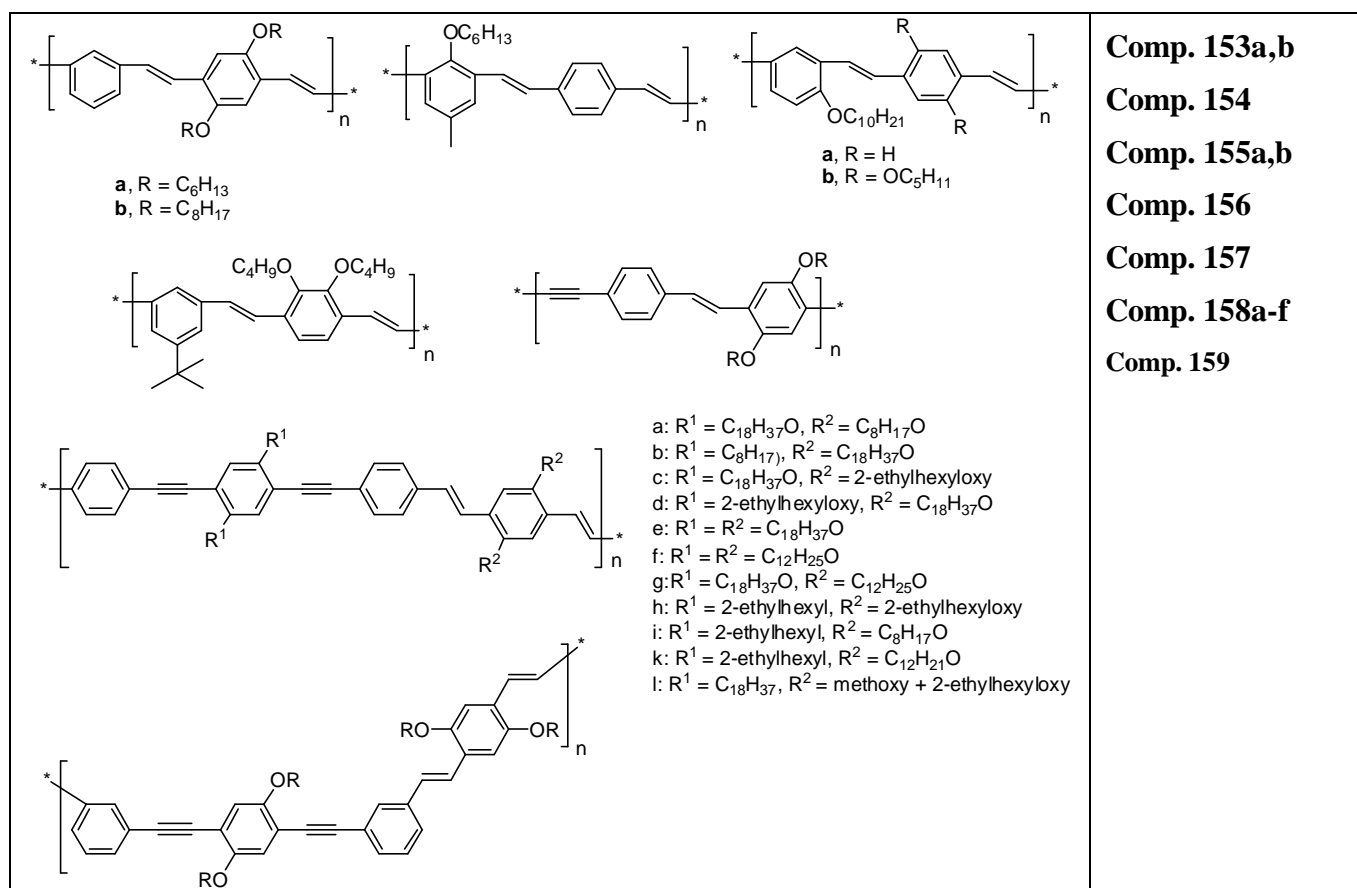
Figure 5. Tuning the electroluminescence in PPV co-polymers through introducing non-conjugated kinks. (a) MEH-PPV **Comp. 13**, (b) **Comp. 147**, (c) **Comp. 150**, (d) **Comp. 152**. [From Ref. 183, © 1999 American Chemical Society].

Almost simultaneously to the above report, Pang et al. reported another PPV co-polymer **Comp. 153a** containing alternating *p*-phenylene and *m*-phenylene units, also synthesized via Wittig-Horner coupling.¹⁸⁴ As expected, **Comp. 153a** exhibits strong hypsochromic shift of the luminescence: in solution the polymer emits blue light with $\lambda_{\text{max}}^{\text{PL}}$ 444 and 475 nm and 60% PL quantum yield, although the later is improved to 82% for the material containing *cis*- defects (these are naturally produced in the synthesis, but can be converted to *trans*- configuration by refluxing in toluene). However, strong aggregation was observed in the solid state, which resulted in shift of the emission maxima to 480 nm and 530 nm (shoulder). In spite of high PL efficiency, the external Q.E. of PLED with **Comp. 153a** was only 0.05% (which still was an order of magnitude higher than that of device with parent PPV **Comp. 1** prepared under the same conditions).

The other structural variations included co-polymers **Comp. 153a,b**,¹⁸⁵ **Comp. 154**,¹⁸⁶ **Comp. 155a,b**,¹⁸⁷ **Comp. 156**.¹⁸⁵ Low switch-on voltage (4.3 V) and moderately high brightness (1,000 cd/m²)

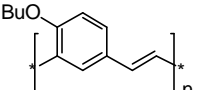
was achieved for **Comp. 155a,b**,¹⁸⁷ but the purity of blue color still was a problem. Even for the “most blue” co-polymer **Comp. 156**, the CIE coordinates ($x = 0.188$, $y = 0.181$) are still quite far from the pure blue emission ($x = 0.15$, $y = 0.06$) due to presence of a green tail.¹⁸⁵

Several groups have studied introduction of phenyleneethynylene unit into PPV backbone. The first material of this type, co-polymer **Comp. 157** was reported by Bunz et al.¹⁸⁸ The material displayed blue luminescence in solution ($\lambda_{\text{PL}}^{\text{max}} = 460$ nm) but due to rigid-rod structure of the polymer, very strong aggregation in the solid state gave rise to bathochromic shift and the PL quantum yield in films was only 5%. A series of poly(phenylene vinylene/ethynylene) hybrids **Comp. 158a-l** have been recently reported by Egbe et al.^{189,190} Whereas all alkoxy-substituted polymers **Comp. 158a-h** showed similar PL emission (λ_{PL} from 525 to 554 nm), the performance of the green-emitting PLEDs thereof ($\lambda_{\text{EL}}^{\text{max}}$ from 508 to 554 nm) strongly depended on the alkyl/alkoxy substituents in the copolymers. For the tested devices of ITO/PEDOT/**Comp. 158**/Ca configuration polymers **Comp. 158a,b** showed somewhat higher turn-on voltage (12–16 V) than other polymers of this series (7–8 V). Drastical change on substituents was observed in external Q.E. of EL for polymers **Comp. 158a-c,e** as low as 0.02–0.047 % for polymers **Comp. 158a-c,e** to 0.89–0.95 % for polymers **Comp. 158d,e**. Similar large differences observed in maximum luminous efficiency (0.085–0.20 cd/A and 3.5–4.0 cd/A, respectively). Reported by Pang, Karasz et al. related polymer **Comp. 159** possesses *m*-phenylene linking groups, which might reduce the aggregation effect (although this was not investigated). The PLED device ITO/PEDOT/**Comp. 159**/Ca was reported to emit green light with external Q.E. 0.32%.¹⁹¹



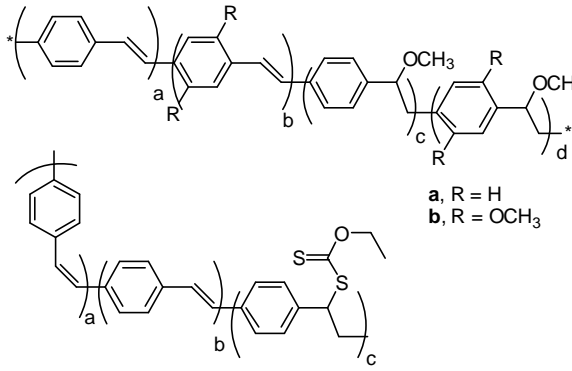
Very recently, Liang et al. reported the first poly(*m*-phenylene vinylene) homopolymer **Comp. 160**.¹⁹² Due to all-meta linking of the phenylene units, the PL maxima (417 nm with a shoulder at 434

nm) of **Comp. 160** is further shifted in the blue region, and the emission band is very narrow, which promises to deliver a pure blue-emitting PLED (although the device fabrication was not yet reported).

	Comp. 160
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1.5.2. Conjugated/nonconjugated PPV block co-polymers

Soon after the first demonstration of the electroluminescence of PPV **Comp. 1**¹ it was shown that introducing saturated (non-conjugated) defects into PPV chain results in blue-shift of the emission and improves the film quality.^{23,25} This could be achieved via modified Wessling-Zimmerman thermoconversion of a precursor polymer containing different (tetrahydrothiophene and methoxy) leaving groups, which can be selectively eliminated to give conjugated and non-conjugated (uneliminated) fragments (**Comp. 161**).^{23,134,193} Similar effect was obtained by controlled conversion of PPV precursor having ethylxanthate leaving group (**Comp. 162**).²⁵ For the later, the ethylxanthate group also favored the formation of cis-vinylene defects, preventing the intermolecular stacking effect (Figure 6). Due to very negligible crystallinity and good film-forming properties, the polymers **Comp. 161** and **Comp. 162** showed significantly improved EL efficiency (the external Q.E. of 0.44% was demonstrated for the device ITO/**Comp. 162**/PBD/Al).^{23,25} Introduction of non-conjugated fragments (by partial substitution of the tetrahydrothiophenium leaving group in the PPV precursor **Comp. 2** with acetoxy group) was also demonstrated to increase the operation life-time of the PLED (above 7,000 h without noticeable degradation).¹⁹⁴

 <p>a, R = H b, R = OCH₃</p>	Comp. 161 Comp. 162
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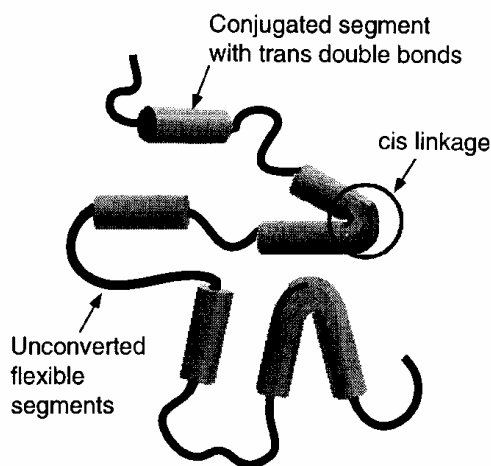


Figure 6. The schematic structure of rigid/flexible block PPV containing saturated (unconverted) units and meta-vinylene links. [From ref. 25, © 1995 American Association for the Advancement of Science].

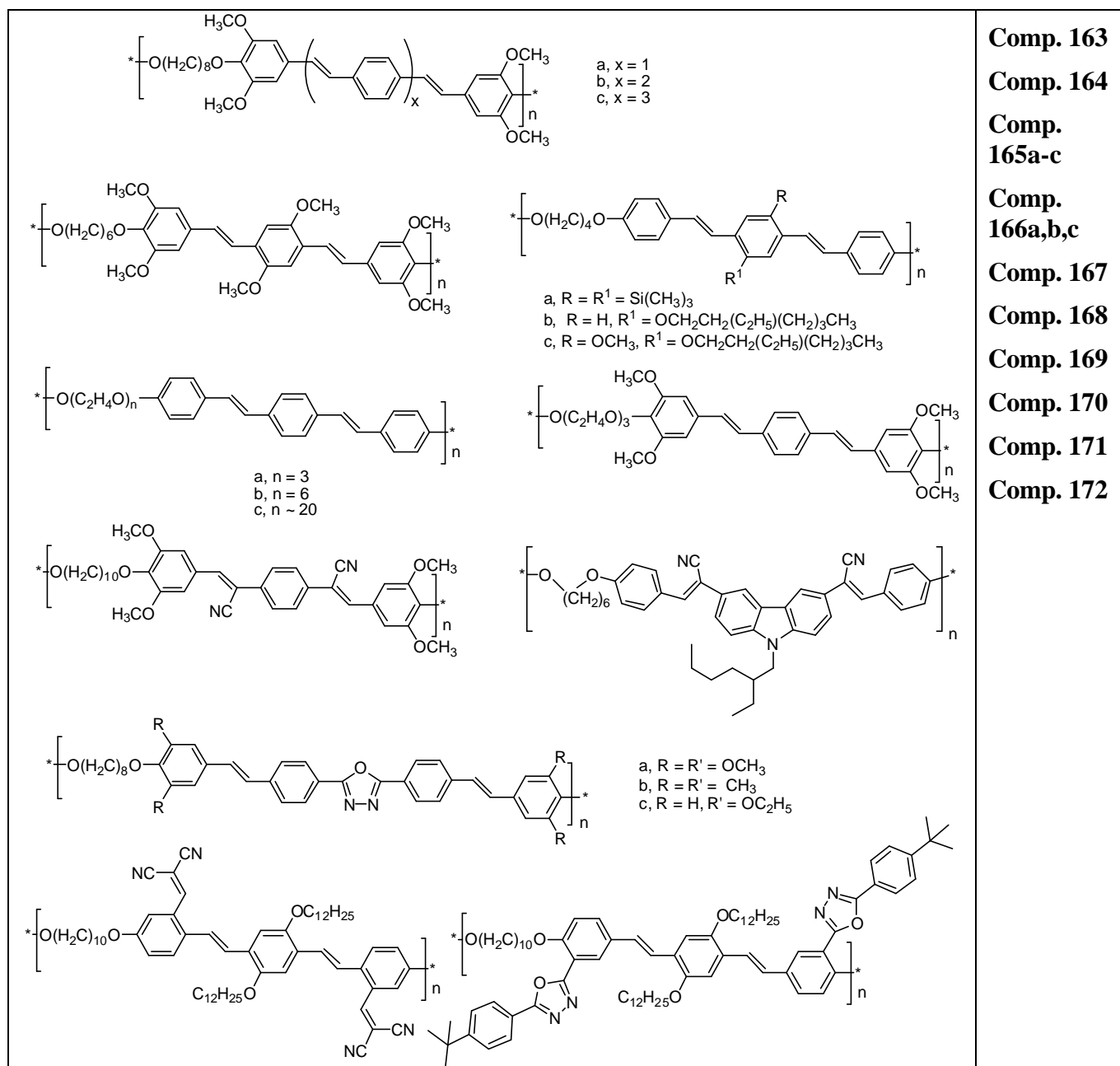
However, due to random distribution of the conjugated length in these polymers, the emitted light was still essentially green. In 1993 Karasz et al. came up with idea of preparing PPV co-polymer, containing well-defined blocks of rigid conjugated oligo(phenylene vinylene) and flexible nonconjugated aliphatic units.¹⁹⁵ Co-polymer **Comp. 163a**, synthesized by Wittig-Horner condensation, contained 2.5 phenylene vinylene fragments in each conjugated block and showed the photo- (and electro-) luminescence maxima at ~465 nm. This low wavelength emission is achieved exclusively due to very short conjugation length, and increasing the later by only one more phenylene vinylene unit (**Comp. 163b**¹⁹⁶ and **Comp. 163c**¹⁸⁶) shifts the emission to $\lambda_{\text{max}} = 513$ nm, so as the PLED ITO/**Comp. 163b**/Al emits green light with CIE coordinates $x = 0.29$, $y = 0.47$.¹⁹⁶ Sun et al. have reported a dimethoxysubstituted analogue **Comp. 164**.¹⁹⁷ The alkoxy substituents in the conjugated block result in a red shift of the emission maxima (vibronic band with peaks at ~ 500 nm, 540 nm and 590 nm [shoulder]) but, remarkably, the PL quantum yield in the solid state was as high as 90%. Several other block co-polymers of this type (**Comp. 165a-c**) having shorter nonconjugated block and different substituents in the phenylene vinylene unit have been synthesized.¹⁹⁸ The trimethylsilyl substituted polymer **Comp. 165a** showed the most blue photo- (and electro-) luminescence ($\lambda_{\text{max}}^{\text{PL}}$ 467, 490 nm), whereas alkoxy substituents result in bathochromic shift of the emission band.

The solubility of such PPV co-polymers in both polar and non-polar media can be dramatically improved when using the oligo(ethyleneoxide) flexible block (co-polymer **Comp. 166**), which also allows the application in LEC. The first compound of this series co-polymer **Comp. 166c** was synthesized by Sandman et al. using low polydispersity polyethyleneglycol block (PEG-900) but no high performance PLED could be fabricated with this material.¹⁹⁹ Later, Feast et al. reported synthesis of co-polymer **Comp. 166b** as a (bluish)green emitter with $\lambda_{\text{max}}^{\text{EL}}$ at 490 and 525 nm and moderately high PL quantum yield (34%).²⁰⁰ The PLED ITO/**Comp. 166b**/Al can be turned on at 6.5 V and shows luminescence efficiency of 0.5 cd/A, and the maximal brightness of 2,000 cd/m².²⁰⁰ Furthermore, the LEC design⁶³ (blending with LiOTf electrolyte) allows to decrease the turn-on voltage to 3.8 V. A more pure blue color with a single emission peak at 490 nm has been reported later with a similar compound **Comp. 166a** having shorter nonconjugated block. The PLED turn-on voltage achieved with **Comp. 166a** is lower (4.6 V) due to more complex device structure (ITO/PEDOT/**Comp. 166a**/Alq3/Ca), but the device efficiency and brightness was very similar.²⁰¹ Alkoxy substituents have

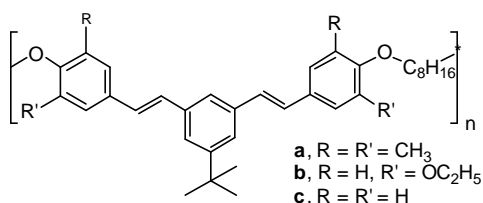
been introduced in this polymer structure but the resulting co-polymer **Comp. 167** showed no improvement of the EL properties ($\lambda_{\text{EL}} = 475$ nm, maximal brightness 36 cd/m² at 23 V).²⁰²

Introducing two cyano groups into the conjugated block (co-polymer **Comp. 168**²⁰³ and **Comp. 169**¹⁵⁶) slightly alters the emission color ($\lambda_{\text{max}}^{\text{EL}} = 493$ nm for **Comp. 168** and 518 nm for **Comp. 169**) but also significantly improves the electron transport properties of the polymer. Nevertheless, even the double layer (ITO/**Comp. 1**/**Comp. 168**/Al) PLEDs showed a modest luminescence efficiency of 0.17 cd/A and maximal brightness of only 40 cd/m².¹⁵⁶ Significantly higher brightness (2,400 cd/m²) and external Q.E. of 0.1% was achieved for PPV block co-polymer **Comp. 169** containing electron-acceptor oxadiazole moiety in the backbone, although extending the conjugation through the oxadiazole moiety also resulted in some red shift of the emission maxima ($\lambda_{\text{max}}^{\text{EL}} = 480\text{--}509$ nm, depending on R).²⁰⁴

Electron-acceptor dicyanovinyl and oxadiazole substituents have been recently introduced into phenylene units of the PPV block co-polymers (**Comp. 171**, **Comp. 172**).²⁰⁵ Blue and blue-greenish PL emission was observed for **Comp. 171** and **Comp. 172**, respectively, but the PL quantum yield was relatively low even in solution (13 and 24%) and no EL device has yet been reported.

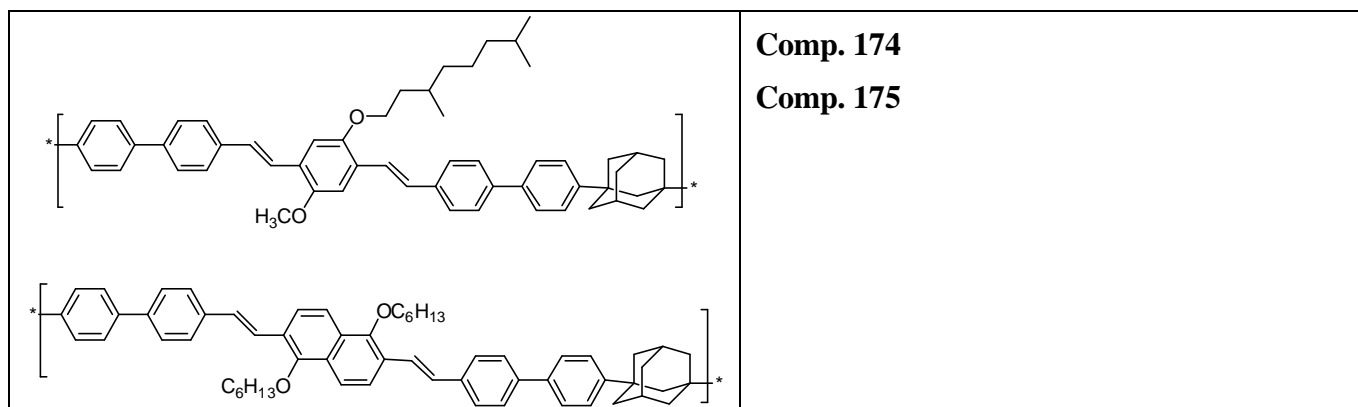


Lahti, Karasz et al. reported a series of meta-linked oligo(phenylene vinylene) block co-polymers **Comp. 173a-c**.²⁰⁶ A meta-linked phenylene unit imposed an additional hypsochromic shift on the emission of these segmented polymers. The PL maxima were found at 399–416 nm, but a significant (ca. 70 nm) red shift was observed for electroluminescent spectra (ITO/polymer/Ca/Al).

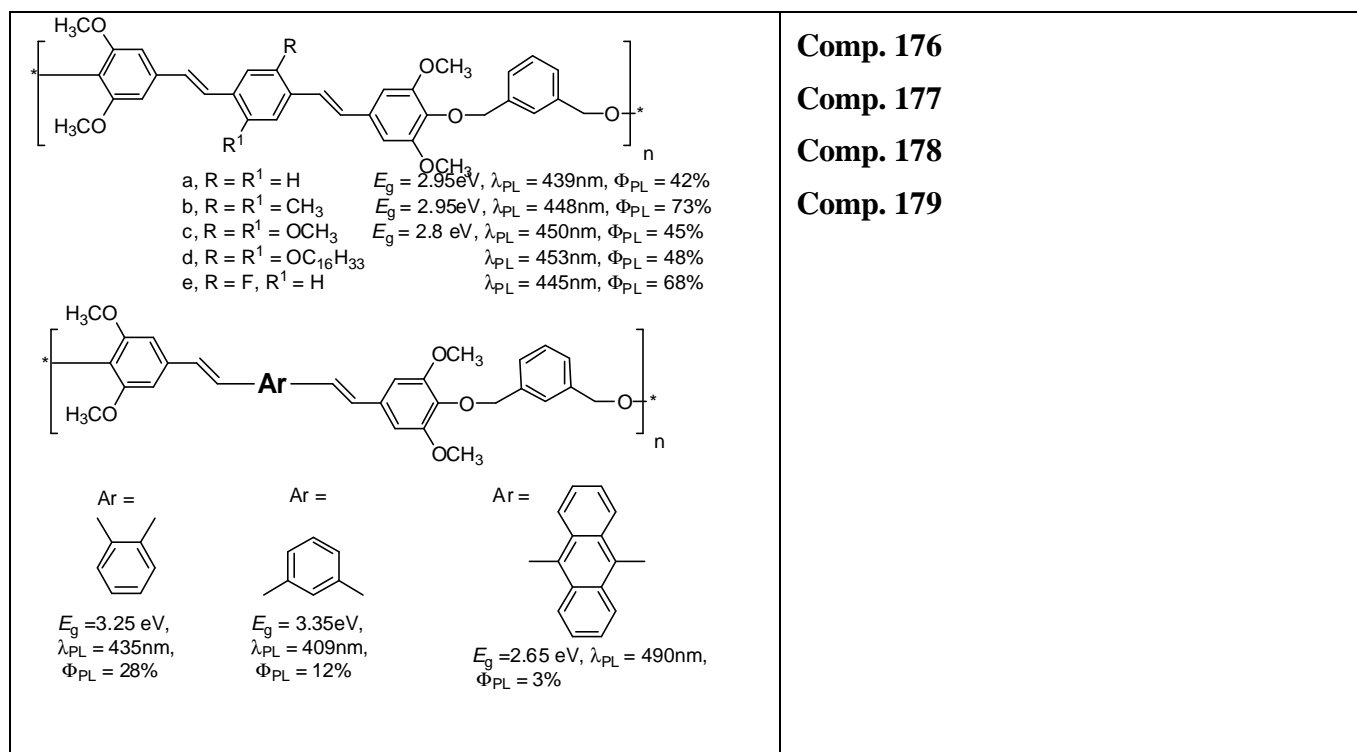


Comp. 173a-c

A research group at Kodak used a rigid adamantane moiety to separate the luminescent oligo(phenylene vinylene) blocks (co-polymers **Comp. 174**, **Comp. 175**).²⁰⁷ The EL color can be tuned from blue ($\lambda_{\text{EL}} = 470$ nm) to green ($\lambda_{\text{EL}} = 516$ nm) by replacing a phenylene unit in **Comp. 174** for 2,7-naphthylene (**Comp. 175**). Very low turn-on voltage of 5.5 V (as for this class of materials) was achieved in the device ITO/**Comp. 174**/Mg:Ag, but no EL efficiency data was reported.



Karasz et al. have also synthesized a series of block co-polymers **Comp. 176–Comp. 179** having a *m*-xylenedioxy bridge as a flexible unit and studied their optical and electrochemical properties.²⁰⁸ Changing the substituents in the central ring of the phenylene vinylene block (polymers **Comp. 176a–e**) or altering the conjugation by changing the aromatic unit in **Comp. 177–Comp. 179**, the emission band can be tuned between $\lambda_{\text{max}}^{\text{PL}}$ 413 and 533 nm (Scheme 20, Figure 7). Breaking the conjugation in the oligophenylenevinylene block by changing the substitution position (1,4-phenylene \rightarrow 1,2-phenylene \rightarrow 1,3-phenylene \rightarrow 9,10-anthracene units) progressively increases the band-gap of the polymer, and hypsochromically shifts the emission band (the longest wavelength absorption and emission peaks of **Comp. 179** are due to isolated anthracene unit; based on the second (phenylene vinylene) absorption band, its $E_g = 3.6$ eV). However, PL efficiencies of compounds **Comp. 177–Comp. 179** also drops down very significantly (Scheme 20), and no EL devices have been reported for this series.



Scheme 20. Tuning the band-gap and the emission wavelength in PPV block co-polymers **Comp. 176–Comp. 179**.

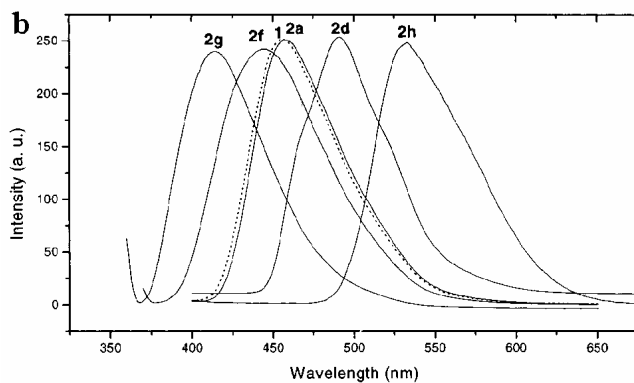
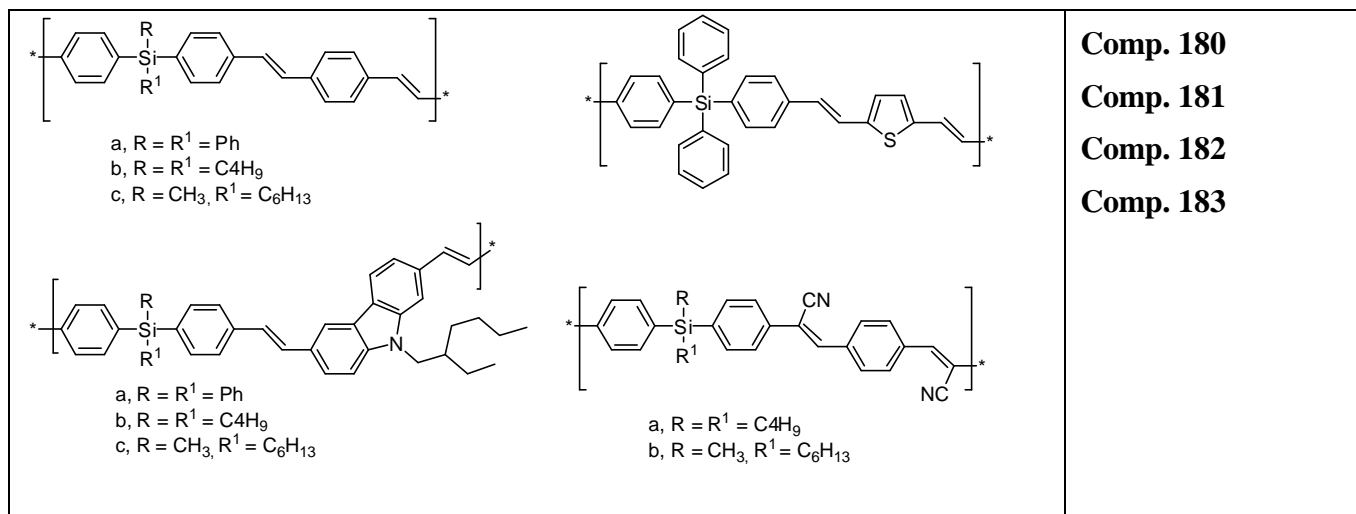
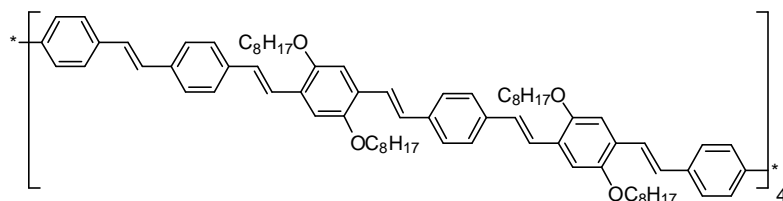


Figure 7. Tuning the emission maxima in PPV block co-polymers **Comp. 176–Comp. 179**. 1 – **Comp. 163**, 2a – **Comp. 176a**, 2d – **Comp. 176d**, 2f – **Comp. 177**, 2g – **Comp. 178**, 2h – **Comp. 179**. [From Ref. 208, © 2000 American Chemical Society].

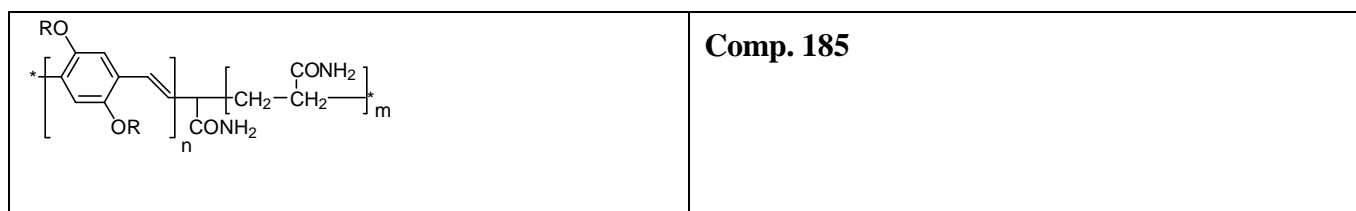
Kim et al. have introduced silicon atom in the PPV block co-polymer to confine the conjugation length and achieve blue color EL material. Co-polymers **Comp. 180–Comp. 182**²⁰⁹ and **Comp. 183**²¹⁰ have been synthesized by Wittig-Horner and Knoevenagel coupling, respectively. The emission band in this series can be tuned between 410 and 520 nm, and ITO/polymer/Al PLEDs with turn-on voltages ~7 V have been reported.



Monodisperse analogues of such π -electron systems, PPV oligomers (so called “molecular glasses”) have been studied by Bazan et al.²¹¹ The films prepared from **Comp. 184** by solution technique showed completely amorphous structure due to a tetrahedral structure of the molecule and OLEDs ITO/PVK/**Comp. 184**/Al emitted green light with external Q.E. up to 0.22 cd/A.

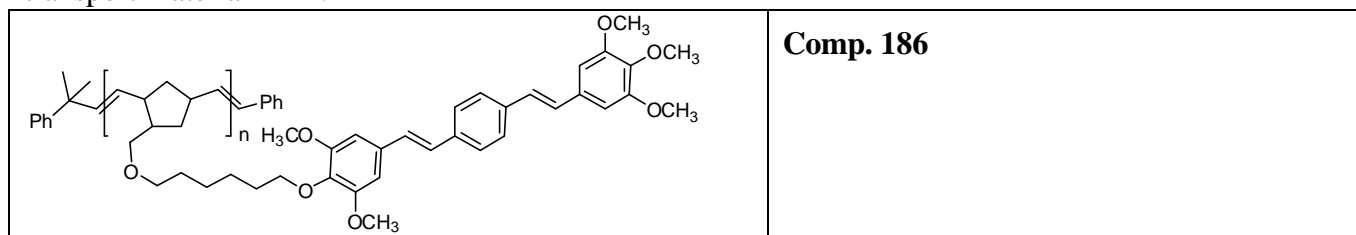
**Comp. 184**

As we discussed above, non-conjugated blocks in PPV co-polymers generally improve the film homogeneity. Furthermore, changing the properties of the non-conjugated blocks one can engineer the topology of the films. Introducing highly polar amide groups into non-conjugated blocks Zhang et al. prepared water-soluble co-polymer **Comp. 185** ($\lambda_{\text{max}}^{\text{PL}} = 509$ nm) which achieves nanophase separation of conjugated and nonconjugated domains in spin-coated films.²¹²

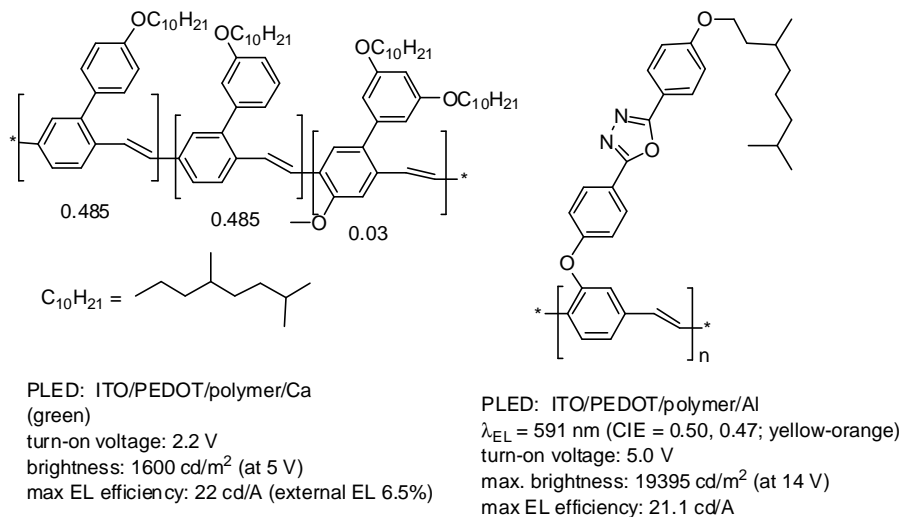


1.5.3. Non-conjugated polymer containing oligo(phenylene vinylene) pendant substituents.

The conjugation length and the emission color of PPV-type materials can be also controlled by using short oligo(phenylene vinylene) units as pendant substituents in non-conjugated polymer chain. The advantage of such approach is possibility to use well-established polymerization techniques, developed for non-conjugated systems for the last century. Thus, Schrock, Friend et al. reported on high-yield (95%) synthesis of a well-defined polymer **Comp. 186** ($n \approx 50$, PDI = 1.1) as a blue-emitting material [$\lambda_{\text{PL}}(\text{films}) = 475$ nm].²¹³ A single layer PLED ITO/**Comp. 186**/Ca showed external Q.E. of 0.3%



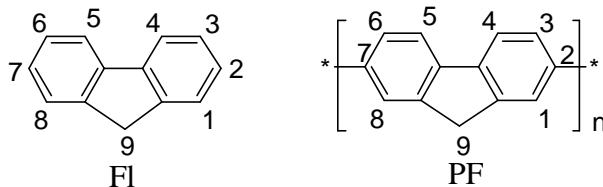
Thus, as we have seen, 15 years of chemical design in PPV materials, together with remarkable engineering progress, resulted in creating of polymer LEDs of remarkable performance. The efficiencies in excess of 20 cd/A was achieved for polymers **Comp. 88**¹⁴⁰ and **Comp. 68**¹²⁴ (Scheme 21), which renders them among the best performing green and orange electroluminescent polymers. Low operating voltages, even with Al cathode, was achieved for PPV-based materials via introduction of electro-accepting fragments. The color tuning in wide range, covering from blue to near-IR region, was demonstrated in PPV co-polymers. The life-time of the PPV-based PLEDs surpasses 20,000 h (for low brightness of ca. 100 cd/m²).



Scheme 21. Best performing PPV electroluminescent polymers **Comp. 88**¹⁴⁰ and **Comp. 68**¹²⁴.

2. Polyfluorenes (PFs)

Fluorene (Fl) is a polycyclic aromatic compound, which received its name due to strong violet fluorescence which arises from highly conjugated planar π -electron system.



The 2,7-Positions in Fl are the most reactive sites towards electrophilic attack, which allows construction of a fully conjugated rigid-rod polymer chain by substitution reactions, whereas the methylene bridge provides an opportunity to modify the processability of the polymer by substituents, without perturbing the electronic structure of the backbone. The varieties, excellent optical and electronic properties, and high thermal and chemical stability of polyfluorenes (PFs) make them an attractive class of materials for polymer light-emitting diodes (PLEDs). Different aspects of syntheses, properties and LED applications of fluorene-based conjugated polymers and co-polymers have been highlighted in several recent reviews.^{214,215,216,217,218,219,220,221} In fact, polyfluorenes are the only class of conjugated polymers that can emit a whole range of visible colors with relatively high quantum efficiency.

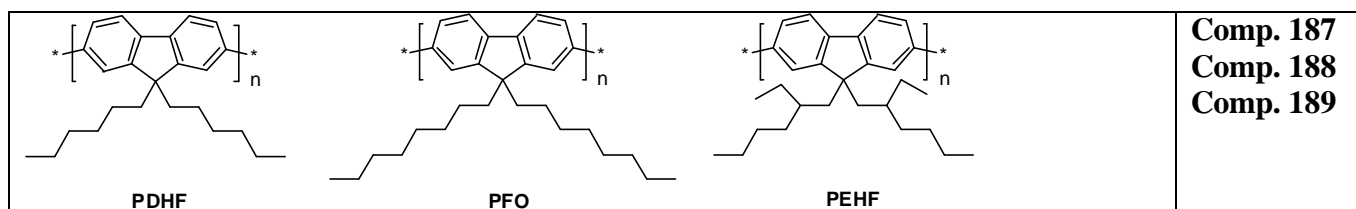
2.1. Characterizations, stability and phase behavior

Routine gel permeation chromatography (GPC) and size exclusion chromatography (SEC) with calibration against polystyrene standard are common methods for estimation of the molecular weights of PF. The PF homopolymers and co-polymers obtained by different synthetic procedures, as will be described below, could substantially differ in molecular weight and polydispersity index, which also depends on the purification procedure. Generally, the M_n ranges from 10,000 to 200,000 with PDI \approx 1.5–3, using polystyrene as a standard,

In principle, both GPC and SEC with polystyrene standard overestimate the molecular weight of PFs because of their rigid-rod character.²¹⁹ Bradley et al. determined an overestimation factor of 2.7 for poly(9,9-dioctylfluorene) by comparing the M_n values of coupled GPC/light scattering with those of the GPC with polystyrene standard.²²² Dynamic light-scattering experiments on narrow fractions (PDI = 1.22 to 1.67) of poly(9,9-bis(2-ethylhexyl)fluorene-2,7-diyl), prepared by preparative GPC fractionation have also displayed reduced absolute M_w values (50–70 %), compared to polystyrene-calibrated SEC results.²²³ Nevertheless, use of GPC and SEC with the same polystyrene standard throughout majority of publications on PFs allows comparing more or less adequately the data for different polymers.

Generally, fluorene homo- and co-polymers show excellent thermal stability: the decomposition temperature (T_{dec}) of many PF exceeds 400 °C (according to TGA analysis under inert atmosphere).²¹⁸

Whereas poly(9,9-dihexylfluorene) (PDHF, **Comp. 187**) is generally considered as amorphous, some PFs with larger alkyl side chains – dioctyl (PFO, **Comp. 188**)^{224,225,226} or bis(2-ethylhexyl) (**Comp. 189**),²²⁷ as well as some fluorene copolymers²²⁸ show liquid crystalline behavior, opening a possibility to fabricate polarized LEDs^{218,229,230}



PFO **Comp. 188** is clearly crystalline with a melting point temperature around 150 °C, above which a nematic mesophase exists up to ca. 300 °C. **Nanoscale** crystallinity of PFO **Comp. 188** was demonstrated by X-ray diffraction (XRD) experiments (**Figure 8**).^{231,232} For the crystalline phase, a periodicity in the plane of the surface of 4.15 Å corresponded to half the fluorene ring repeat distance along the backbone.^{233,231} Octyl chains (which are perpendicular to the direction of PF backbone) of two neighboring polymer backbones is believed to intercalate allowing a more efficient space filling. This side chain packing may be responsible for an unusual ability of PFO **Comp. 188** and related PF to undergo thermotropic alignment into monodomain structures.²³³ PFO **Comp. 188** is the most studied PF for its crystallinity and liquid crystallinity (LC) having the largest effects and most promising properties for polarized EL, although both LC and crystallinity were also reported for **Comp. 187**.^{231,234} It was also shown that high degree of alignment in PFO **Comp. 188** can be achieved by the friction-transfer technique with subsequent thermal treatments; depending on cooling rate liquid-crystalline or crystalline films are formed.²³⁵

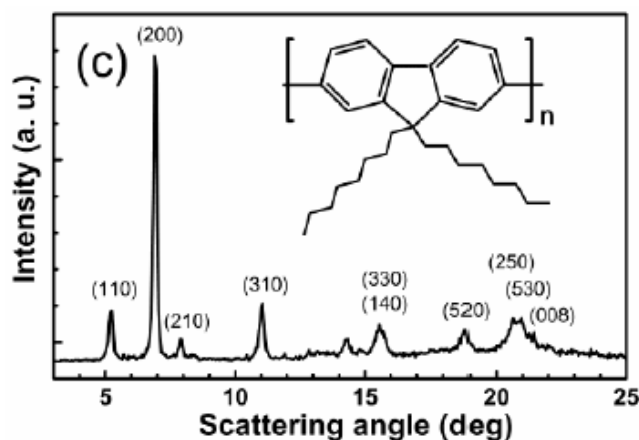


Figure 8. **Low-angle** XRD of highly crystalline thick-film PFO **Comp. 188** specimen after extended heat treatments at elevated temperatures and stepwise cooled to room temperature (From **Ref. 231**; © 2004 American Chemical Society).

Several reports on studies PF with optically active side chains imply helical nature in the fluorene chain (right- or left-handed 5/2 and 5/1 helical states).^{236,237,238,239} Because of high tendency of PF to form ordered structures solvent could have a large effect on the morphology and photophysical properties of PF films and consequently device performance. Bradley et al showed dramatic changes in the absorption spectra of PFO **Comp. 188** resulting from certain treatment protocols (dissolution in moderately poor solvent such as cyclohexane, or exposing spin-coated films to toluene or THF vapor).²⁴⁰ Sirringhaus et al demonstrated that the highest degree of macroscopic order was observed in films that were cast from an aromatic solvent and annealed while still “wet”, which was attributed to the plasticizing effect of the solvent during the reorientation process.²⁴¹ This ordering did not directly correlate with the boiling point of the solvent and **was especially poor** in films cast from chlorinated

solvents. These results demonstrate that the choice of the solvent and casting/drying/annealing techniques is very important for the device performance.

2.2. Optical and Electronic Properties

The electronic absorption spectra of dilute (typically 5–10 mg/L) solutions of poly(9,9-dialkylfluorenes) show a sharp peak with $\lambda_{\text{max}} \sim 385\text{--}390\text{ nm}$ (3.2 eV) of $\pi\text{--}\pi^*$ electronic transition. The thin solid films (spin-coated from 15–20 mg/mL solutions) reveal similar absorption with slightly red-shifted ($\sim 10\text{ nm}$) and a relatively broader peak (due to intermolecular interaction) (Figure 9).

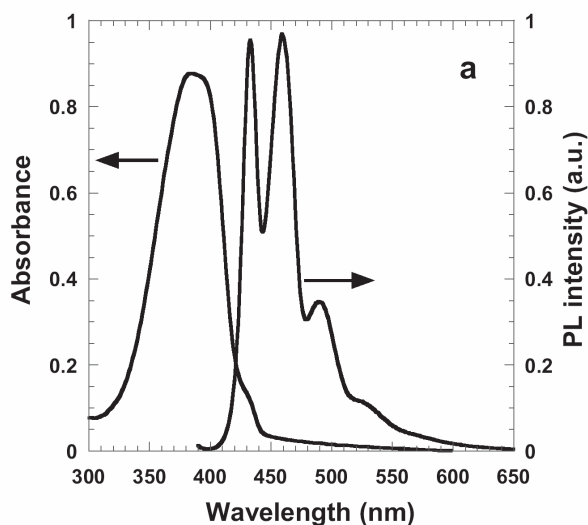


Figure 9. Typical absorption and emission spectra of polyfluorene in thin films (shown for poly(9,9-dioctylfluorene **Comp. 188**). [From Ref. 242, © 2001 Wiley-VCH].

The photoluminescent spectra of the PFs show well-resolved structural features with maxima at 420 nm, 445 nm, and 475 nm, assigned to the 0-0, 0-1, and 0-2 intrachain singlet transition, respectively (the 0-0 transition being the most intense).²⁴³ Due to the tail emission spectrum of PFs, the thin films emit bright sky-blue light. The quantum efficiency (Q.E.) of the PFs is very high, typically in the range of 40% to 80% and, as shown for PFO **Comp. 188**, it depends substantially on the morphology of the polymer.²⁴⁴

The effective conjugation length, estimated for poly(9,9-dihexylfluorene) **Comp. 187** from the absorption maxima of a series of monodisperse oligofluorenes (isolated from the mixture of oligomers by HPLC) is *ca.* 11.8 fluorene units (Figure 10).²⁴⁵ The conjugation length of 9–10 fluorene units was deduced from optical band gaps (i.e., red-edge of absorbance) in oligo(9,9-dihexylfluorenes) ($n = 1\text{--}5$).²⁴⁶

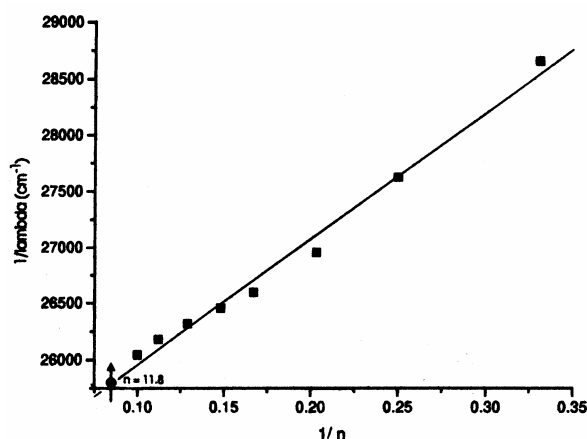


Figure 10. Plot of $1/\lambda_{\max}$ vs. $1/n$ for oligo(9,9-dihexylfluorenes) **Comp. 187** in tetrahydrofuran (n is the number of fluorene units); • is for the polymer with degree of polymerization of 54, the absorption maximum of which (388 nm) corresponds to effective conjugation length $n = 11.8$. [From Ref. 245, © 1998 American Chemical Society].

Similar estimation of the conjugation length for **Comp. 189** ($\lambda_{\max} = 383$ nm) from the linear dependence of $1/\lambda_{\max}$ vs. $1/n$ for oligomers with $n = 2-7$ gave the conjugation length of 14 repeated units.²⁴⁷

The band gap, determined as the onset of absorption band in thin films is 2.95 eV (425 nm). Janietz, Bradley and co-workers used the on-set of the redox bands in cyclic voltammetry experiments to estimate the I_P and E_A energies of the dialkyl-PFs (Figure 11).²⁴⁸ The gap between the obtained energy levels (5.8 eV for I_P and 2.12 eV for E_A) $I_P - E_A \sim 3.8$ eV is substantially higher than the optical band-gap. Although, of course, the optical absorption and electrochemistry tests two physically different processes (vertical electron excitation and adiabatic ionization) and are not expected to be the same, very good agreement between both methods have been documented, particularly, for conjugated polymer systems. On the other hand, the I_P/E_A values derived from the electrochemical measurements in films should be taken with great caution, since they are often obtained under non-thermodynamic conditions (irreversible or quasireversible redox process) and may include a very significant kinetic factor, due to structural re-arrangements and counter-ion diffusion. This is confirmed by comparison of the redox potential of PF in thin films and in solution, where the solution experiments gave significantly lower band gap, similar to the optical band gap.²⁴⁹

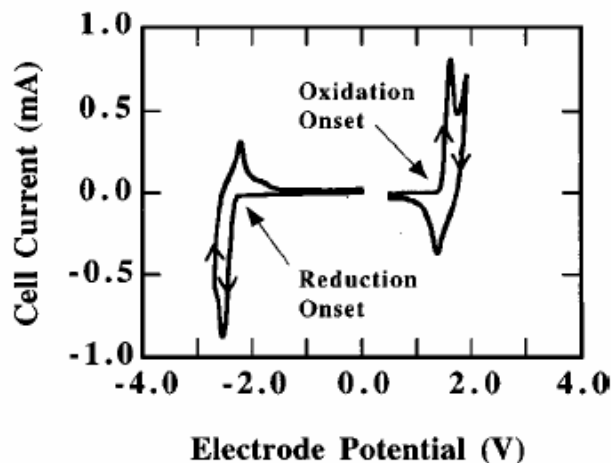


Figure 11. Cyclic voltammetry of PFO **Comp. 188** in thin film (potentials vs. Ag/AgCl). [From Ref. 248, © 1998 American Institute of Physics].

The ultraviolet and X-ray photoelectron spectroscopy (UPS/XPS) measurements find the I_p of the PFO at -5.6 ± 0.05 eV, and the band gap at 3.1 ± 0.1 eV, which is also much closer to the optical band-gap than to the value deduced from the electrochemistry in films.²⁵⁰ Thus, the HOMO/LUMO levels of the PF can be reasonably well matched by workfunctions of ITO/PEDOT (-5.1 eV) and Ca electrode (ca. -2.9 eV), respectively. However, as shown by Lee et al.²⁵¹ the energy levels of the PF can be shifted significantly in contact with active metals as Ca, and should be taken with caution. It was also shown that an initially nonohmic PEDOT/PFO **Comp. 188** contact in ITO/PEDOT/ PFO/Al device can be made locally ohmic by electrical conditioning of the device at voltages higher than the EL onset voltage.^{252,253} Ohmic injection of holes was also observed from plasma-cleaned ITO electrode or ITO electrode coated with PEDOT (for fluorene-triarylamine copolymer **Comp. 244**).²⁵⁴ The possibility of tuning the HOMO/LUMO energy levels in PF is very important. Besides affecting the emission color, it facilitates the hole/electron injection (and also mobility) by matching the work functions of the electrodes, and thus improves the device performance.

Beside the excellent optical properties and suitable HOMO/LUMO energy levels, the PF's possess great charge transport properties. The time-of-flight (TOF) measurements of PFO showed nondispersive hole transport with a room temperature mobility of holes of $\mu_+ = 4 \times 10^{-4}$ cm²/V s at a field of $E = 5 \times 10^5$ V/cm that is ca. one order of magnitude higher than that in PPV.²⁵⁵ The polymer revealed only a weak field dependence of the mobility, from $\mu_+ = 3 \times 10^{-4}$ cm²/V s at $E = 4 \times 10^4$ V/cm to $\mu_+ = 4.2 \times 10^{-4}$ cm²/V s at $E = 8 \times 10^5$ V/cm.

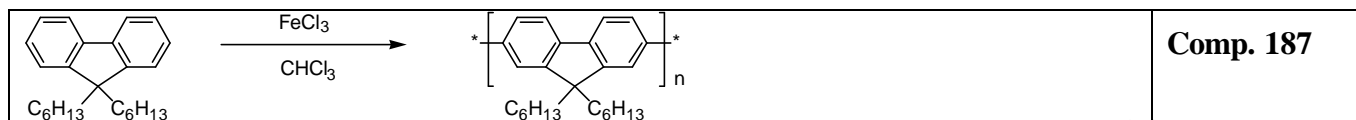
Because of a great importance of PF as a class of conjugated polymers with excellent optical and electronic properties, several theoretical studies were performed to better understand the electronic structure and the photophysical processes, which occur in these materials.^{256,257,258,259,260,261}

2.3. General methods in synthesis of PF homopolymers.

The parent (unsubstituted) PF was first synthesized electrochemically by anodic oxidation of fluorene in 1985²⁶² and electrochemical polymerization of various 9-substituted fluorenes was studied in detail after that.^{263,214} Cyclic voltammogram of fluorene ($E_{red}^1 = 1.33$ V, $E_{ox}^2 = 1.75$ V vs. Ag/Ag⁺ in acetonitrile²⁶³) with repetitive scanning between 0 and 1.35 V showed the growth of electroactive polyfluorene film on the electrode with an onset of the p-doping process at ~ 0.5 V (vs. Ag/Ag⁺). The unsubstituted polyfluorene was an insoluble and infusible material and was only studied as possible material for modification of electrochemical electrodes. For this reason, it is of little interest for electronic or optical applications, limiting the discussion below to the chemically prepared 9-substituted polyfluorenes.

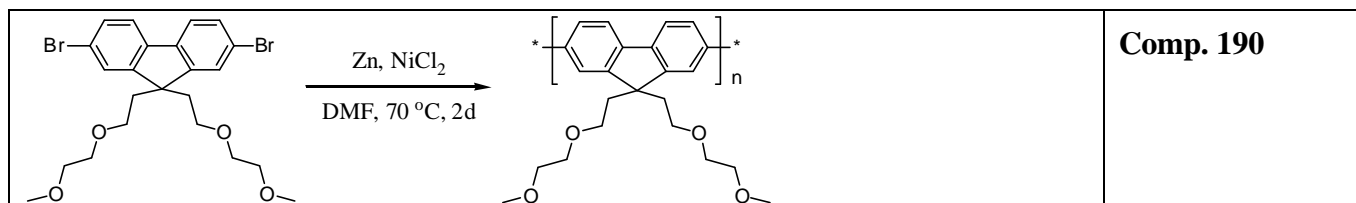
The first synthesis of poly(9,9-dialkylfluorene) with long-chain solubilizing hexyl groups (**Comp. 187**) was carried out by Yoshino's group via oxidative coupling reaction using ferric chloride in chloroform (Scheme 22).^{264,265} This resulted in polymers with relatively low molecular weights (M_n up to 5,000). The regioregularity of the polymerization process in these conditions was rather poor due to non-regiospecific oxidation reaction resulting in some degree of branching and non-conjugative linkages through the positions other than 2 and 7. Some evidence of irregular coupling along the backbone was shown by NMR of soluble low-molecular weight fraction.²⁴³ The PLED fabricated using this material gave relatively low Q.E., and, in spite of a well-resolved vibronic structure of PL band, the EL emission showed a very broad band (maximum at 470 nm).²⁶⁶ A serious drawback of this synthetic

method was also a significant amount of residual metal impurities, which dramatically affected the PLED performance.



Scheme 22 Oxidative coupling synthesis of poly(9,9-dihexyl)fluorene **Comp. 187**.²⁶⁴

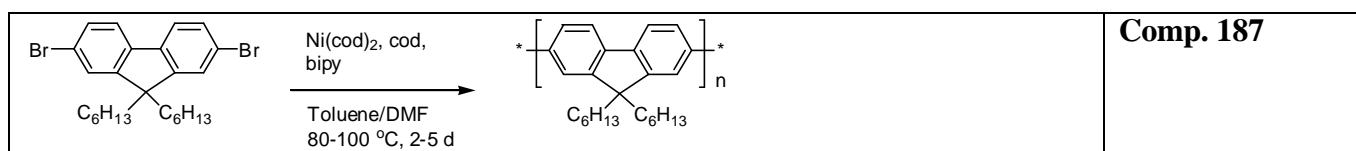
The next step towards soluble PF as materials for PLEDs, was an application of Yamamoto synthesis to polymerize various 2,9-dihalo-9,9- R^1, R^2 -fluorenes. Pei and Yang at Uniax Corporation first reported a reductive polymerization of 9,9-bis(3,6-dioxaheptyl)fluorene in DMF using zinc as a reductant and reactive $Ni^{(0)}$ as a catalyst (generated from $NiCl_2$ salt) resulting in high molecular weight PF **Comp. 190** ($M_n = 94,000$ vs. polystyrene standard, PDI = 2.3), (Scheme 23).²⁶⁷ However, the patent application from Dow Chemical Co describing polymerization of various 9,9-disubstituted 2,7-dihalofluorenes, halo = Br or Cl, by the same Yamamoto synthesis in similar conditions was filed almost a year before that, in July 1995.²⁶⁸ Later on, numerous patents from Uniax^{269,270} and Dow Chemical^{271,272,273,274} described preparation of various PF by Yamamoto synthesis.



Scheme 23 First Yamamoto synthesis of synthesis of poly[9,9-bis(3,6-dioxaheptyl)fluorene].²⁶⁷

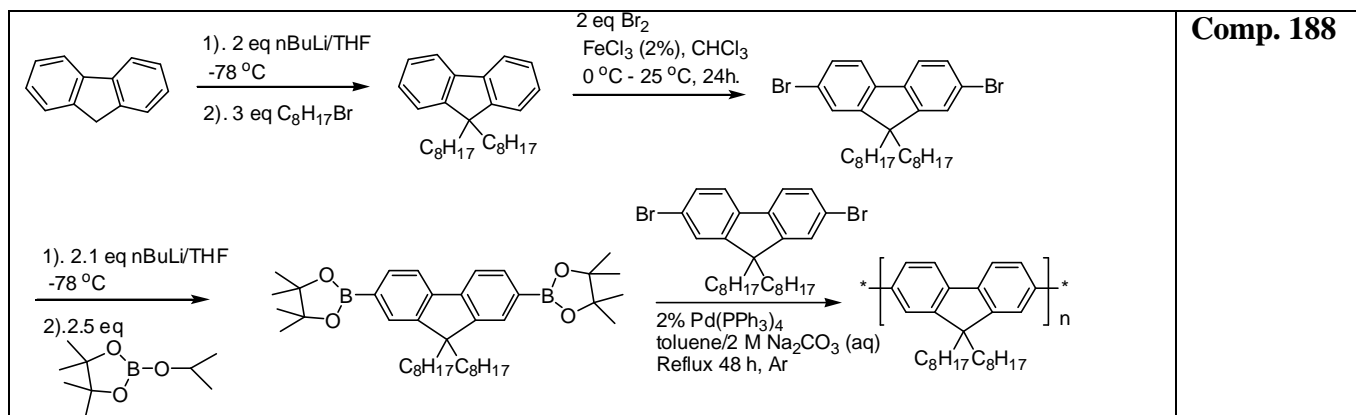
Although Ni-catalyzed reaction allowed improvement of the regiospecificity and minimization of cross-linking and mislinking reactions²⁴³ as compared to $FeCl_3$ oxidation method, it employs large amount of metals (Ni, Zn) during the synthesis and resulting polymer should be carefully purified from the metal impurities. In addition, because of the non-polar hydrophobic nature of poly(9,9-dialkylfluorenes), the polymer chain growth in polar solvents (DMF, DMA), which are used in $Zn/NiCl_2$ reductive polymerization is terminated by the polymer precipitation from the reaction mixture, limiting the molecular weight. Thus, whereas relatively high molecular weight $M_n = 94,000$ can be achieved for PF **Comp. 190**, containing hydrophilic 3,6-dioxaheptyl substituents, in the cases of various alkyl substituents the molecular weights are limited to $M_n \sim 14,000\text{--}60,000$.^{268,269,270,271}

Another example of Yamamoto-type polycondensation²⁷⁵ was demonstrated by Miller et al.^{276,245} who performed coupling of corresponding 2,7-dibromofluorenes using $Ni(cod)_2$ /cyclooctadiene/2,2-bipyridyl in toluene-DMF solvent mixture (Scheme 24). This method allows preparation of PFs with very high molecular weight M_n up to 250,000 (i.e. up to ~ 500 fluorene units),²⁷⁷ and Scherf and List noted²¹⁹ that on the lab scale the usage of $Ni(cod)_2$ as reductive transition metal-based coupling agent is very convenient.



Scheme 24 Synthesis of PF by Yamamoto coupling with $Ni(cod)_2$.

Suzuki-coupling synthesis of PF, first reported by Leclerc et al.,^{278,279} could minimize the problem of metal impurities by employing catalytic amount of the $\text{Pd(PPh}_3)_4$ (Scheme 25), and the use of a phase transfer catalyst gives higher molecular weights ($M_n \sim 50,000$ instead 15,000).^{278,279,280} Although the molecular weights of PF achieved by Yamamoto coupling with Ni(cod)_2 (up to $M_n \sim 100,000$ – $200,000$) are higher than those obtained by Suzuki coupling (*ca.* several tens thousands Daltons), reaching such high molecular weights is controlled not only by the method of the coupling but mainly by careful purification of the monomers and by optimization of the reaction conditions, as well as by the solubility of the polymer in the reaction mixture, determined by substituents on the fluorene nucleus.



Scheme 25 Synthesis of PF via Suzuki-coupling reaction.²⁷⁸

Simultaneously and independently researchers at Dow Chemicals filed a patent describing preparation of a wide range of homo- and co-polymers of a series of dialkylfluorenes by Suzuki and Yamamoto-coupling polymerization,²⁷² and an improved technological procedure for Suzuki-coupling polymerization of dialkylfluorenes was also reported by Cambridge Display Technology (CDT).²⁸¹

2.4. The problem of pure blue emission in PFs: excimer/aggregate formation or fluorenone defects?

The major problem in application of PFs in blue PLEDs is color instability. As will be discussed below, the pure blue emission of PFs can be contaminated by undesired contribution of a green emission band (at *ca.* 530 nm) upon thermal annealing of the polymer film and/or during the device operation. The initial hypotheses explained this phenomenon by formation of aggregates²⁸² and/or excimers^{283,284,285,286,287,288}, which act as energy and/or charge traps and emit in the long-wavelength region. Indeed, the green emission increased during the thermal annealing and was not observed in solution of the polymer. This hypothesis born a tremendous amount of synthetic research activities, based on introduction of bulky substituents in the PF side chain or bulky fragments in the backbone of the polymer to prevent the formation of the excimers. Such modifications really resulted in some cases in stabilization of blue emission that was, in turn, classified as confirmation of the hypothesis of excimeric nature of green emission in PF.

More recently, it was shown by List, Scherf and co-workers,^{289,290,291,292} and, later, Moses et al.²⁴² that the green emission of the PFs is due to fluoren-9-one defects in the polymer chain. This was confirmed by comparison of PL films annealed in an inert atmosphere and in air: progressive additional

band in green region was observed on annealing in air (Figure 12).²⁴² Similar increase in green PL peak was observed on photooxidation of the dialkyl-PF **Comp. 191** film (Figure 13).²⁸⁹ IR spectra also indicate on appearance of fluorenone C=O peak at photooxidation^{242, 289} and the same peak in green region appears in EL spectra during the device operation.

The defects can be either introduced on the stage of synthesis or caused by photooxidation during the device preparation and functioning. It was shown that less than 1% of the fluorenone defects can almost completely quench the blue fluorescence of the PF, transferring the excitation energy into the long-wavelength region.²⁹³ Importantly, as confirmed by theoretical calculations,²⁵⁸ the PF chain planarization and dense intermolecular packing facilitate the energy transfer onto the fluorenone defects, which is much less efficient in solutions.²¹⁹ This explains the partial success of the strategy of introducing the bulky substituents, which hinders the energy transfer onto fluorenone defect sites. Moreover, the intensity of long wavelength emission is increased in the electroluminescence spectrum, due to the fact that more electron deficient fluorenone units can act as electron traps, increasing the probability of electron-hole recombination on the fluorenone defects. The polarized emission experiments on partially photooxidized aligned PF films indicate that the emission from the keto-defects exhibits a somewhat smaller polarization ratio than the blue emission from the defect-free chains.²⁵⁹ This observation was explained with a support of quantum-mechanical calculations, which showed that the polarization of the fluorenone emission is influenced by local disorder.²⁵⁹

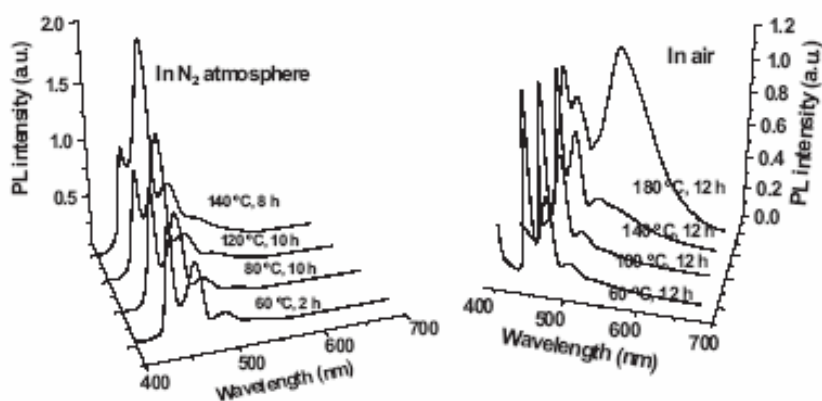


Figure 12. PL spectra of PFO **Comp. 188** films after annealing at different temperatures: a) in a nitrogen atmosphere, and b) in air. [From Ref. 242, © 2003 Wiley-VCH].

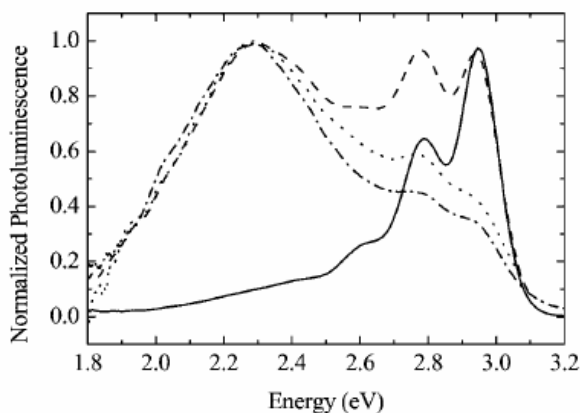
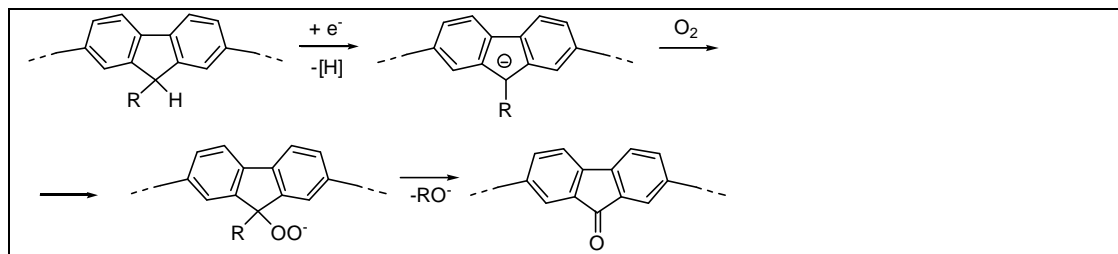


Figure 13. PL emission spectra of a pristine PF **Comp. 191** film (solid line), and after photooxidation with a 1000 W xenon lamp under air for 2 min (dashed line), 4 min (dotted line), and 6 min (dashed-dotted line). [From Ref. 289 ©, 2002 Wiley-VCH].

Zhao et al. studied green emission of poly(9,9-dioctylfluorene) end-capped by polyhedral oligomeric silsequioxanes by PL, photoexcitation, GPC and FTIR spectroscopy.²⁹⁴ They concluded that it originates from the energy traps associated with fluorenone defects, however increased fluorenone concentration is not, by itself, sufficient to account for the increased green-to-blue emission intensity ratio. From studies of FTIR spectra (appearance of new C=C double-bond stretching at 1430 and 1460 cm^{-1} not associated with the aromatic rings *{bullshit}*) they concluded on β -hydrogen elimination in alkyl chains results in C=C alkene fragments, which lead to crosslinking in the polymer. Such a crosslinking apparently enhances excitation energy migration and energy transfer to the traps centers. Another detail studies to understand the origin of green emission was performed by Bradley et al.²⁹⁵ They supported the idea of List et al. on importance of fluorenone defects for the green emission in PF, which, however, on their opinion appears to have its origin in an inter-chain/intter-segment excited-state species and not in the monomeric fluorenone CT π - π^* state proposed by Scherf, List et al.^{289,290,291} On the basis of comparative studies of matrix-isolated PF chains with non-diluted PF films, kinetic of PL decay and effects of molecular fluorenone additions they concluded that green-emission band arises from a fluorenone-based excimers.

Although the exact mechanism of the fluorenone formation is not known, it is believed that the monoalkylated fluorene moieties, present as impurity in poly(dialkylfluorenes) are the sites most sensitive to oxidation. The deprotonation of rather acidic C(9)-H proton by residue on Ni(0) catalyst, routinely used in polymerization or by metal (e.g., calcium) cathode in LED device form very reactive anion, which can easily react with oxygen to form peroxides (**Scheme 26**).²⁸⁹ The latter are unstable species and can decompose to give the fluorenone moiety. It should also be noted that an interaction of low-work-function metals with films of conjugated polymers in PLED is more complex phenomenon and the mechanisms of quenching of polyfluorene luminescence by calcium cathode was studied by Stoessel et al.²⁹⁶



Scheme 26. The mechanism for the generation of keto-defect sites as proposed by List et al.²⁸⁹

Meijer et al. recently demonstrated that the purity of the 9,9-dialkylfluorene monomer is of great importance for the stability of the resulting polymer **Comp. 192**.²⁹⁷ They performed additional purification of the monomer by treatment with potassium *tert*-butoxide in THF (to deprotonate the monoalkylated by-product) with following filtration through dried alumina (twice). The material, obtained by polymerization of thus treated monomer showed significantly less pronounced green emission, as compared to the polymer obtained from unpurified monomer (Figure 14). Furthermore, the device operated for 60 h showed no change in EL spectrum.

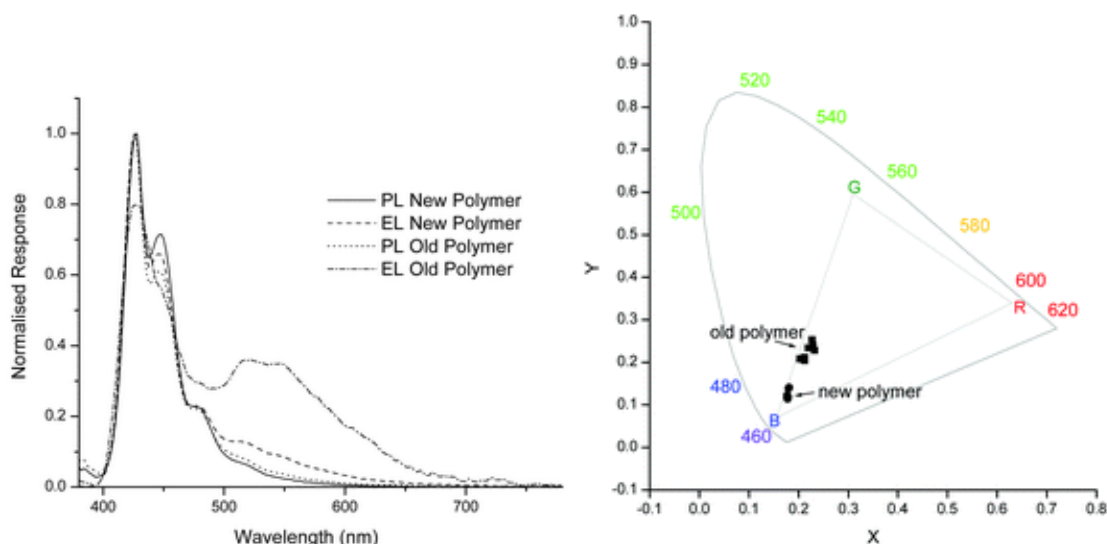
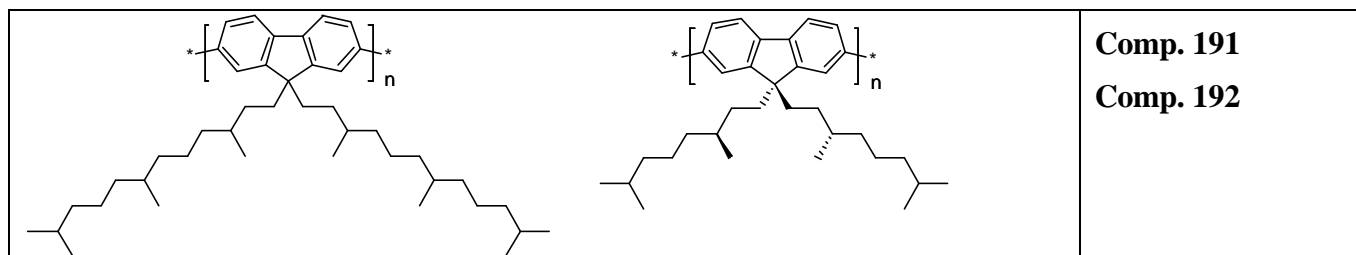


Figure 14. Electro- and photo-luminescence [PL: excitation at 265 nm; EL: at 3.6 V (new polymer, i.e. obtained from purified monomer) and 4.0 V (old polymer, i.e. obtained from conventional monomer)] spectra of **Comp. 192** (left) and CIE (1931) x - y color coordinates of old (squares) and new polymers (circles) from 4 to 6 V (right). [From Ref. 297, © 2003 The Royal Society of Chemistry].

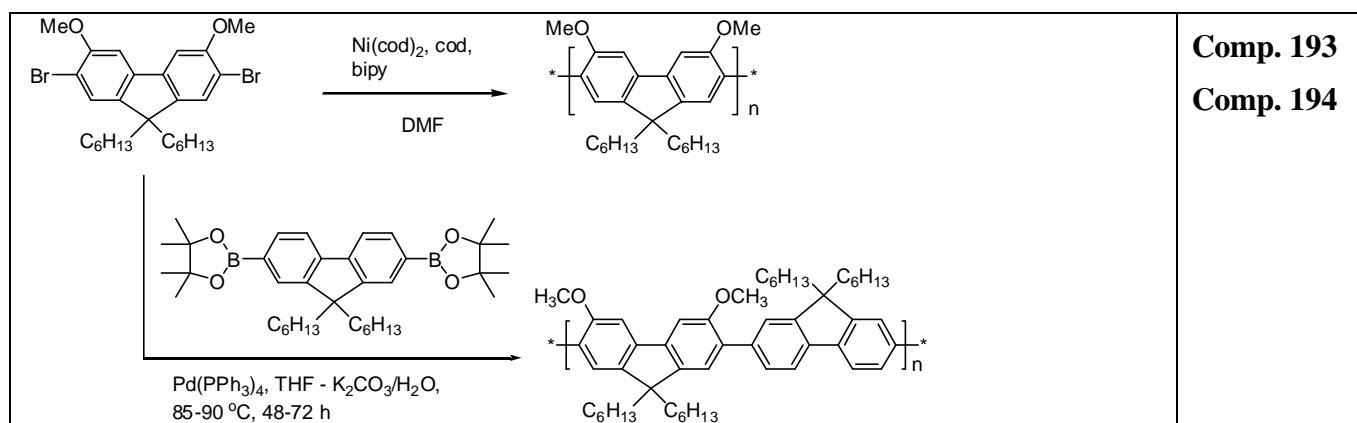
In this context, a recently proposed procedure for alkylation of 2,7-dibromofluorene by alkylbromides in Bu^tOK/THF is advantageous over the widely used alkylation in aqueous NaOH or KOH as it could directly result in more pure monomers with good yields (see Appendix).²⁹⁸ The reaction can be easily monitored by a color change (from yellow to pink) and it is also more convenient than alkylation using BuLi, due to low cost and ease of handling. In contrast to BuLi, an excess of Bu^tOK can be used to ensure the complete alkylation.

On the other hand, the stability of the dialkylfluorene moiety to photo/electrooxidation cannot be postulated as well. The n -doping of PF (chemically, from Ca cathode, or electrochemically during the device operation) forms radical-anion species (see, e.g. theoretical studies of the effect of PF doping with Li atoms²⁵⁶), which are not expected to be stable towards oxygen. Thus, not only monomer/polymer purification, but also the device structure/operation should be optimized in order to achieve pure blue emission. In this line, Moses et al. have shown that introducing a buffer layer between the PF and the cathode (Ca) layers block the metal diffusion in the polymer, and inhibit the fluorenone defects formation, which improves the color stability during the device operation.²⁴²

The following sections will discuss the modifications of the chemical structure of PF through introduction of side chain substituents and end-capping units, co-polymerization with other conjugated units and polymer blends, aiming to achieve a pure blue light-emitting polymer. After that, tuning of the emission color via polyfluorene backbone change and charge/energy transfer process will be discussed.

2.5. Aromatic ring-substituted PF.

Almost all modifications in PF homopolymers consist of variation of substituents at position 9 of the fluorene nucleus. Recently Beupré and Leclerc reported a new synthetic strategy to polymers **Comp. 193** and **Comp. 194** with the aim to modulate the I_p of the PFs (for better injection of holes from the anode in LED) by introducing donor 3,6-dimethoxy substituents into the fluorene moiety (**Scheme 27**).²⁹⁹ The Φ_{PL} of the polymer **Comp. 193** is relatively low (48%), but it can be increased to 93% by introducing a dihexylfluorene co-monomer unit (co-polymer **Comp. 194**), which is probably due to partial release of the steric hindrances brought by 3,6-substituents.



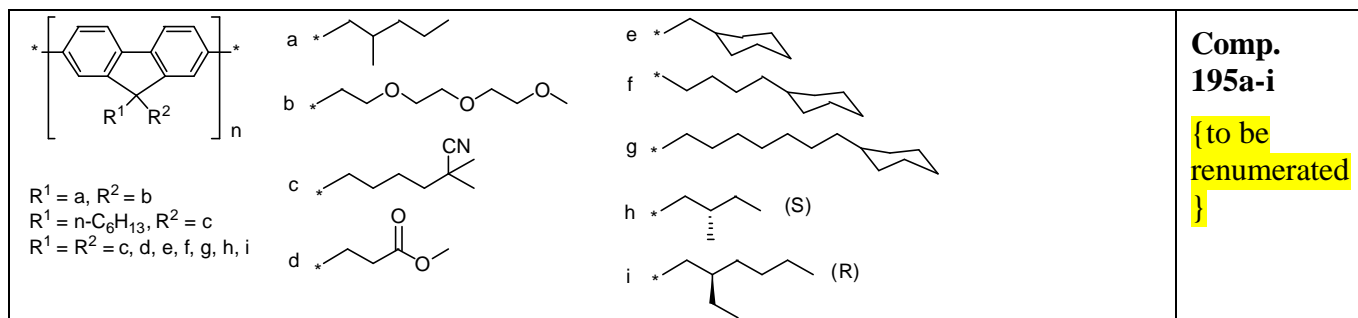
Scheme 27. Synthesis of PFs with 4,5-dimethoxy substituents in the fluorene rings.

2.6. Side-chain modifications in PF.

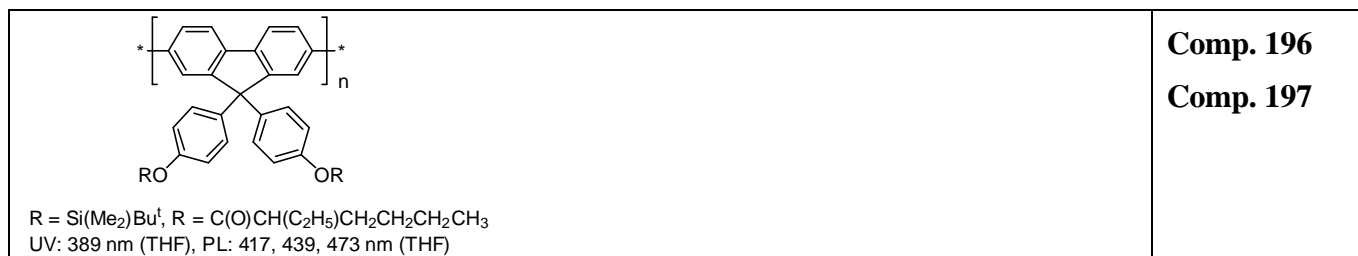
Many studies on side-chain modifications in PF were initially based on the idea of the main role of excimer formation in appearance of undesired green emission in EL spectra during the LED operation or in solid state PL on annealing PF films. This determined several proposed strategies in design of fluorene side-chain homopolymers, where bulky side substituents at position 9 of the fluorene moiety should sterically prevent (hinder) interchain interaction in PF and thus improve the stability of blue emission.

The group of Miller at IBM investigated the intensity of the long-wavelength emission in 9,9-dialkyl-PFs with different length alkyl chains.³⁰⁰ Interestingly, DSC analysis reveals that while dihexyl-PF **Comp. 187** is amorphous, dioctyl-PF **Comp. 188** and even branched poly(9,9-bis(2-ethylhexyl)fluorene) **Comp. 189** are crystalline. Photoluminescent spectra of the polymer thin films show the appearance of green emission band during the thermal annealing (appearance of long wavelength emission) regardless of the crystallinity of the films, although the effect was somewhat less pronounced for polymers with larger substituents (**Comp. 188** and **Comp. 189**).

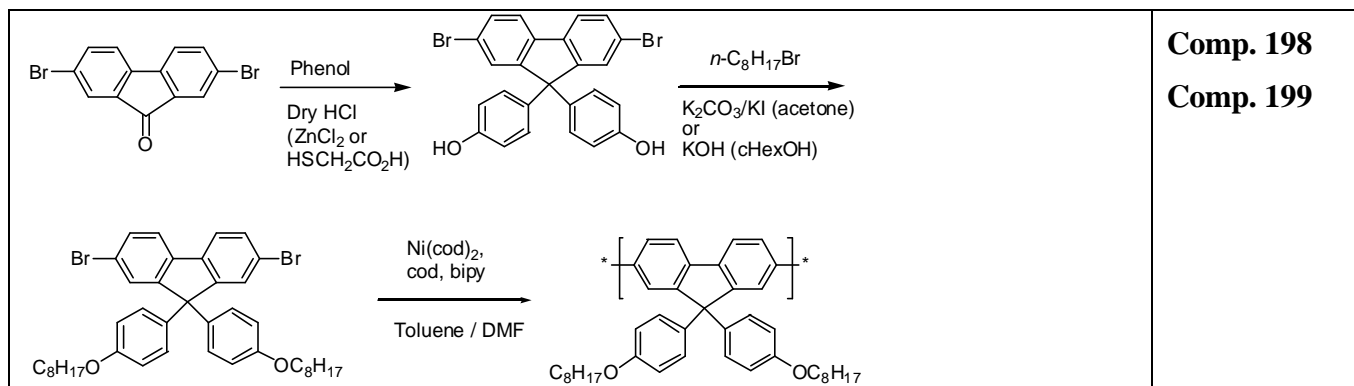
In addition to already mentioned **Comp. 187**–**Comp. 192**, many other alkyl substituents and their derivatives have been introduced at 9-position of the fluorene nucleus in order to create a processable stable blue emitting PF material, e.g. **Comp. 195a-i**.^{269,270,271,301} Chiral substituted polyfluorenes **Comp. 192**, **Comp. 195i** have been synthesized to study their chiroptical properties,³⁰² interest to which particularly supported by polarized emission in such materials.



Patents of Dow Chemicals first described 9,9-diarylsubstituted PF homopolymers **Comp. 196**, **Comp. 197** by Yamamoto polymerization of corresponding 2,7-dibromo monomers,²⁶⁸ although the methods for the monomers preparation were not described. For unsubstituted fluorenone, a convenient methods of its conversion into 9,9-(4-hydroxyphenyl)-^{303,304,305} and 9,9-(4-alkoxyphenyl)fluorenes³⁰⁶ were reported previously, which included condensation of fluorenone with phenol or its ethers in acidic conditions (dry HCl^{304,305} or H₂SO₄^{303,307}) in the presence β -mercaptopropionic or mercaptoacetic acids. Both polymers **Comp. 196** and **Comp. 197** showed similar $M_n \sim 21,000$ with PDI of 1.48 and 1.75, respectively, and spectral data typical for PF [**Comp. 197**: $\lambda_{\text{abs}} = 389$ ($\epsilon = 50,000 \text{ M}^{-1} \text{ cm}^{-1}$); $\lambda_{\text{PL}} = 417, 439, 473 \text{ nm}$ (THF)].



Polymer **Comp. 199** obtained by Yamamoto polymerization of monomer **Comp. 198** (Scheme 28)³⁰⁷ showed bright blue emission with PL maximum in a film at 430 nm. Its emission was found to be very stable towards thermal annealing. In contrast to poly(9,9-dialkyl)fluorenes,²⁴² this polymer did not show green component in the PL spectrum after annealing for 2 h at 180 °C in air (Figure 15), and FTIR spectra also did not show carbonyl peak after annealing indicating on good resistance of the polymer against oxidation.³⁰⁷ The device ITO/PEDOT/**Comp. 199**/Ca/Al showed turn-on voltage of 3.7 V ($\sim 1 \text{ cd/m}^2$), with a maximum luminance of 820 cd/m^2 and EL efficiency of 0.03 cd/A (CIE: $x = 0.136, y = 0.162$). Similar increased stability of pure blue emission towards thermal annealing (as compared to dialkyl-PF homopolymers) was also observed in random co-polymers of monomer **Comp. 198** with 2,7-dibromo-9,9-di(2-ethylhexyl)fluorene (absorption and PL spectra of which were very similar to those of homopolymers **Comp. 199**). However, these showed somewhat lower values of luminous efficiency and maximum brightness, and slightly increased turn-on voltage.³⁰⁸



Scheme 28. Synthesis of poly[9,9-di(4-octyloxyphenyl)fluorenes].

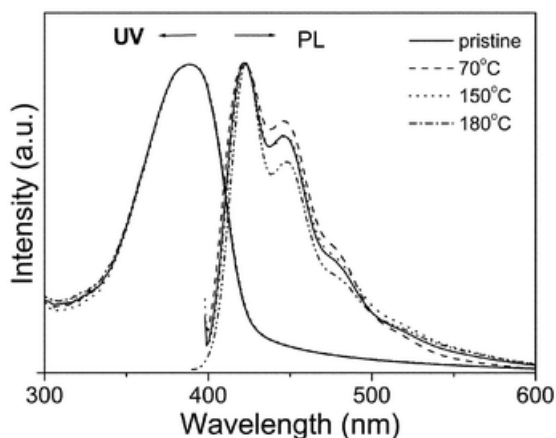
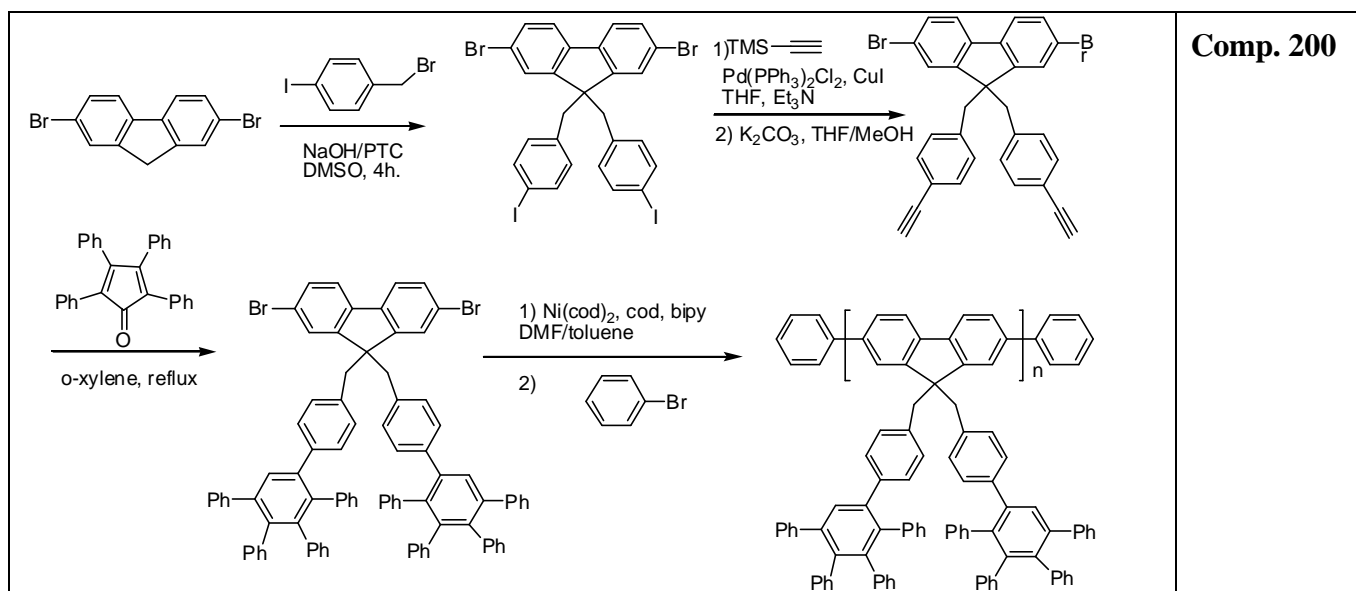


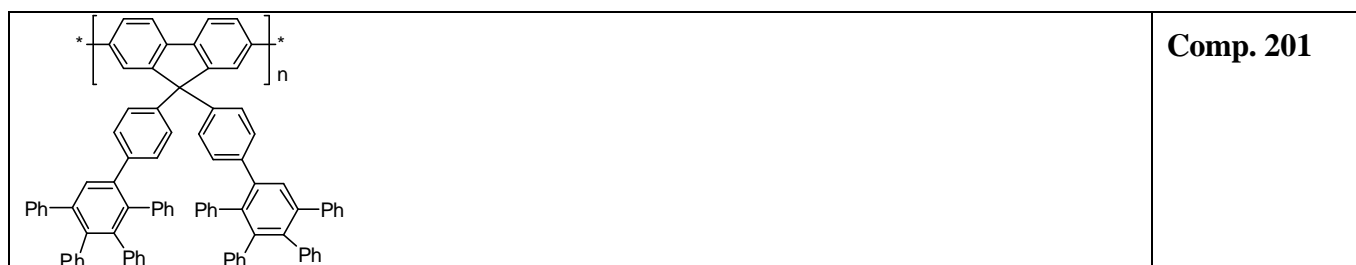
Figure 15. UV-Vis absorption and PL emission spectra of film of **Comp. 199** after thermal annealing for 2 h at different temperatures in air. [From Ref. 307, © 2003 The Royal Society of Chemistry].

Müllen's group at Max-Planck Institute was first to report using dendron substituents to sterically hinder the excimer formation, which deliver pure blue emission of substituted PF material.³⁰⁹ The dendron-contained monomer was obtained from 2,7-dibromofluorene in three elegant steps including base-catalyzed alkylation of the fluorene methylene group followed by Pd(0)-mediated Hagihara-Sonogashira coupling introducing the acetylene functionality, and the Diels-Alder cyclization producing the phenylene dendron (Scheme 29). The polymerization was achieved by Yamamoto coupling and the polymer chain was terminated by arylation with bromobenzene.

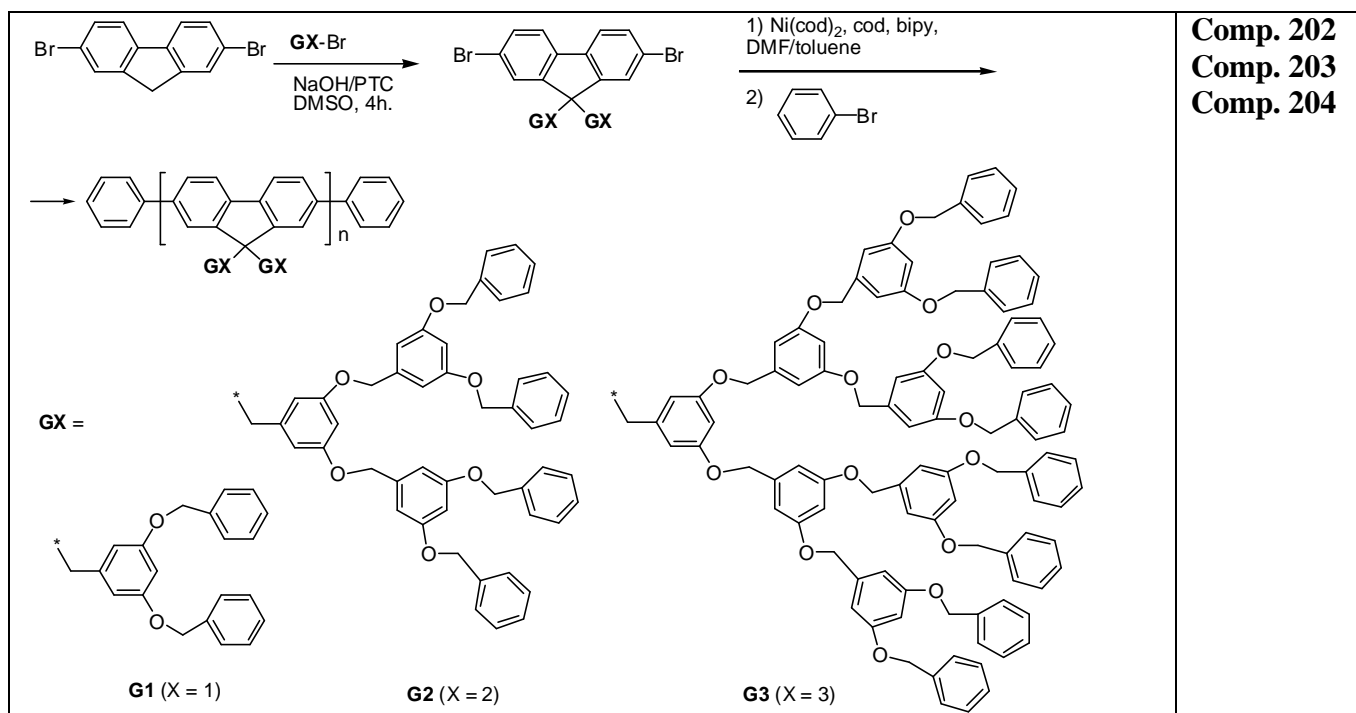


Scheme 29. Synthesis of the phenylene-dendron substituted PFs.

The resulting polymer **Comp. 200** is soluble in toluene, benzene and chlorinated organic solvents and forms high-quality films. The molecular weight was determined by GPC analysis to be $M_n = 46,000$ g/mol (PDI = 3.6), which corresponds to ~40 repeat units. This polymer exhibits the same absorption and emission maxima as alkyl-substituted PFs, which implies that the bulky groups in the 9-position do not alter the torsion angle of the conjugated backbone. Thin films of the oligophenylene-substituted PF emit pure blue color without any tail green emission, even after thermal annealing at 100 °C for 1 day, confirming high impact of dendron substituents suppressing the intermolecular aggregation. PLED device fabricated in the structure of ITO/PEDOT/**Comp. 200**/Ca/Al, gave a pure blue emission, and no green band appeared at driving voltages up to 12 V. However, it was found that the device stability is relatively low due to photooxidation of the benzyl linkage group. This was improved by design of a modified polymer **Comp. 201** having the phenylene dendron attached immediately to the 9-position of PF.³¹⁰



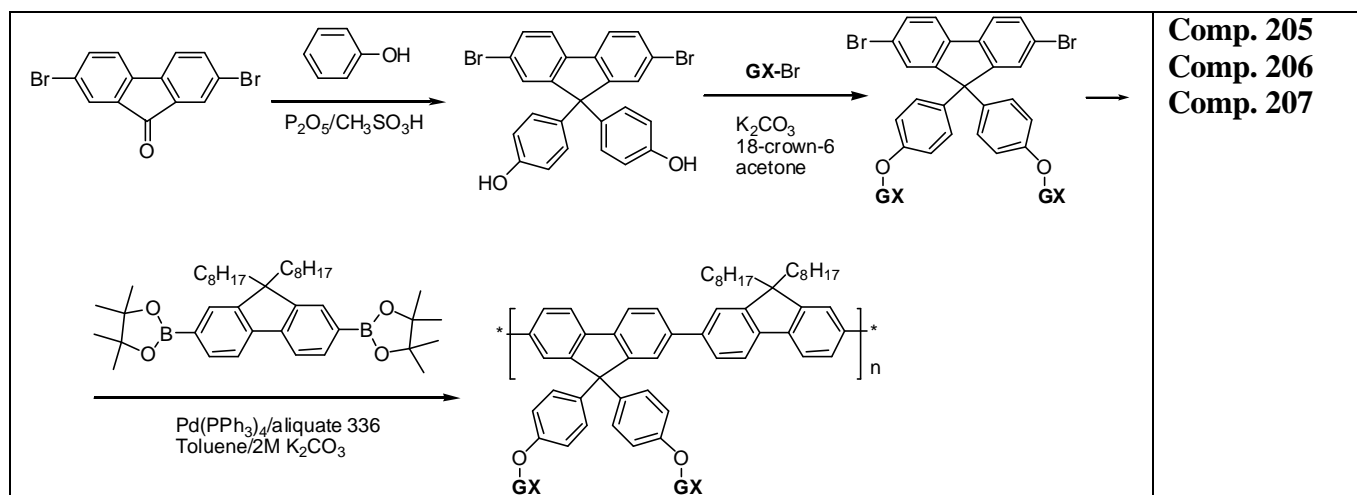
A different type of dendron was used by Carter's group at IBM. They demonstrated significant suppressing of aggregation by inserting ether (Fréchet-type) dendrimer substituents at 9 positions of PFs (Scheme 30).³¹¹ Due to big size and flexibility, these substituents can act as encapsulators of the PF chain, hindering the aggregation and increasing the solubility.



Scheme 30. Synthesis of the Fréchet-type dendrimer substituted PFs.

These dendrimer-contained PFs **Comp. 202–Comp. 204** were synthesized smoothly by Yamamoto polymerization followed by chain termination (end-capping) with bromobenzene. All the polymers were soluble in common organic solvents, and rather high molecular weight ($M_n = 51,400$ g/mol) was found by GPC for the smallest dendron polymer **Comp. 202**. On the other hand, in higher generation dendrimer polymers **Comp. 203** and **Comp. 204** strong steric hindrances inhibit the polymerization, so that only short oligomers ($M_n = 4,400$ – $9,300$, 2–6 units) can be prepared. These polymers show a bright blue fluorescence in solution, with Q.E. comparable to that of alkyl-substituted PF. The effect of dendron substituent is apparent in annealed thin films: while the shortest-substituent derivative **Comp. 202** still exhibits a tail emission in the long wavelength region (540 nm), no such band is seen in the emission of films of **Comp. 203** (polymer **Comp. 204** displayed only a weak fluorescence due to poor film quality, as a result of a very low polymerization degree). A similar trend was also observed in a series of co-polymers of dendron substituted FI with alkyl-substituted FI, but using less sterically hindered co-monomers allows to achieve a high molecular weight polymer with the most bulky dendron. The results indicated that rather bulky dendron substituents (third generation and higher) must be used in order to completely suppress the interchain interaction. Preliminary results show pure blue light luminescence from PLEDs fabricated in configuration ITO/PEDOT/**Comp. 202–Comp. 204**/Ca/Al, with driving voltage of 4.5–16 V (depending on the structure). However, nothing was reported on the stability of the devices, which is expected to be low due to possible (photo)oxidation of CH_2 group, as discussed above.³¹⁰

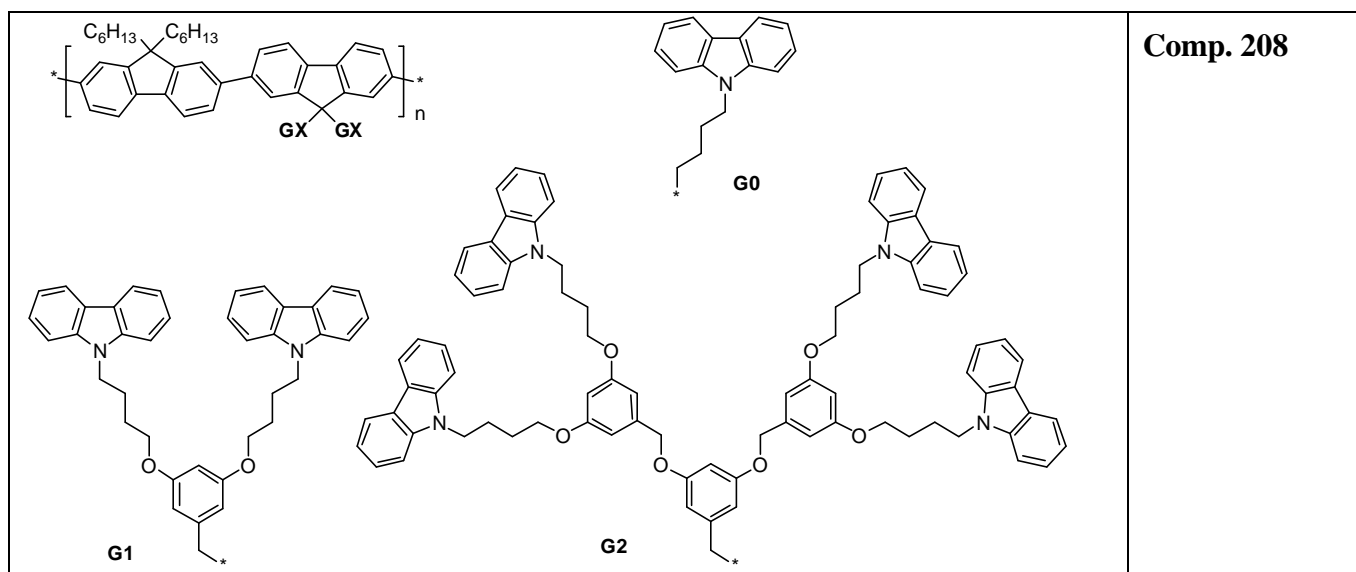
Half a year later, Shu et al. reported Suzuki coupling synthesis of the fluorene co-polymers containing Fréchet-type dendrimers as side chains.³¹² In contrast to the above systems (Scheme 30) in polymers **Comp. 205–Comp. 207** the photooxidizable methylene group is separated from the photoactive PF chain by an additional phenylene moiety. The starting monomer was readily prepared from 2,7-dibromofluorenone by acid-catalyzed arylation with phenol, followed by Williamson alkylation of hydroxy groups.



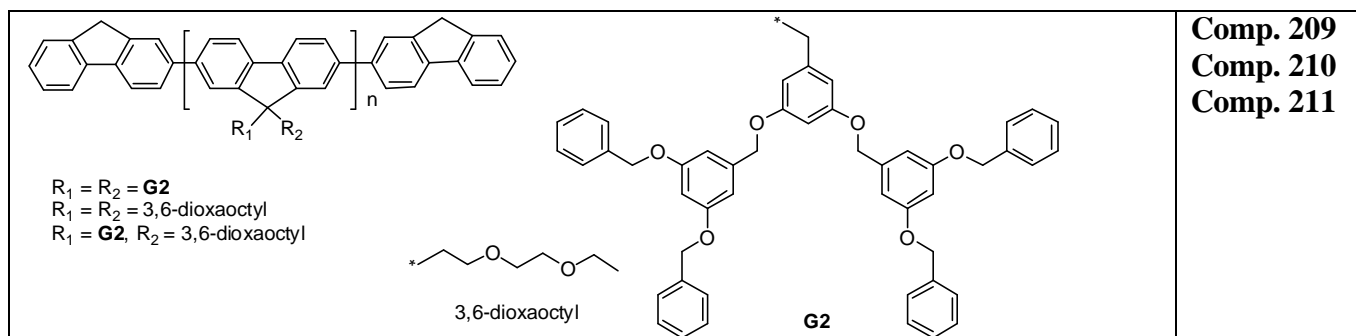
Scheme 31. Dendrimer-PF alternated co-polymer synthesized by Suzuki coupling (same functional groups **GX** as in Scheme 30).

The highly branched dendron-substituted PF co-polymers are readily soluble in common organic solvents. The molecular weights of the three generation co-polymers were in the range of $M_n \approx 1.5\text{--}3.5 \times 10^4$ with polydispersity in the range of 1.9–2.5 (by GPC analysis). The UV-Vis spectra of **Comp. 205** and **Comp. 206** in solution and in thin films showed the same spectra as dialkyl-PFs, but higher hypsochromic shift was observed for **Comp. 207**. The result is the same as previously observed for the high generation dendron-functionalized PFs, and reveals different degree of polymerization. The PL spectra of dendritic PFs **Comp. 205–Comp. 207** exhibited the same emission maxima as PFO **Comp. 188**. The emission spectra of annealed thin films follow the same trend as in homopolymers **Comp. 202–Comp. 204**: the green emission is visible (though suppressed comparing to PFO) for **Comp. 205**, but completely disappears starting from **Comp. 206**. Apart of strong shielding effect, introduction of dendrimer side groups in PFs may also improve the thermal stability of the material, but no LED device performance was reported for these materials.

Recently Bo et al. reported on dendronized PF with carbazole end groups in the peripheral Fréchet-type dendrons **Comp. 208**.³¹³ Polymers emitted blue light with high PLQY of 86–96 % in solution for all three polymers (G_0 – G_2). In the solid state PLQY depended on the size of attached dendron (29, 55 and 64 % for G_0 , G_1 and G_2 , respectively).

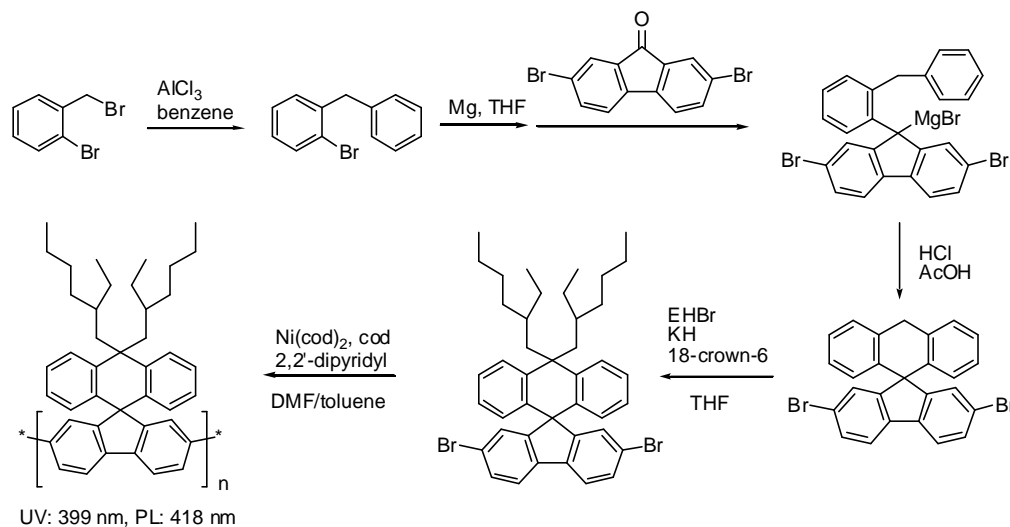


Fujiki et al. synthesized asymmetrically substituted polyfluorenes bearing a bulky Fréchet-type dendron and a less bulky 3,6-dioxaoctyl group in the 9-position.²⁸⁶ The polymers **Comp. 209–Comp. 211** showed a pure blue PL emission with rather low green emission band (at 520 nm) for the films annealed at 200 °C for 3 h (in vacuum).



Furthermore, the green emission band for the films of asymmetric polymer **Comp. 211** was much weaker than that of polymer **Comp. 210** having two straight substituents, and even polymer **Comp. 209**, having two bulky dendron substituents. The latter fact was attributed to liquid-crystalline properties of relatively well-defined polymer **Comp. 209**, comparing to more disordered asymmetrically substituted **Comp. 211**. However, an alternative explanation, by difficulties in complete dialkylation of fluorene with two bulky substituents (to completely convert the oxidizable C–H bonds) should be also taken into account. In the light of fluorenone-origin explanation of the green emission, the terminal end-capping of the polymers **Comp. 209–Comp. 211** with 9-*H*-fluorene is likely to cause the device instability. This is not seen during the annealing *in vacuo* (i.e., in the absence or at least very low concentration of oxygen), but is likely to show up during the operation of the PLED under atmospheric conditions.

Kim et al. reported polyfluorene derivatives **Comp. 212** containing a spiro-dihydroanthracene-fluorene units in which remote C-10 position of anthracene moiety allows a facile substitution with alkyl groups for improving the solubility (Scheme 32).³¹⁴ The polymer showed high spectral stability towards heat treatment, UV irradiation and high current passage. The ITO/PEDOT/**Comp. 212**/LiF/Ca/Ag device showed good color coordinates (CIE: $x = 0.17$, $y = 0.12$) and a maximum luminance of over 1600 cd/m².

Comp. 212

Scheme 32. Synthesis of soluble spiro-anthracene-fluorene polymer.

Another example of spiro-derivatized polyfluorene was demonstrated by Bo et al. who synthesized soluble spirobifluorene-based polymer **Comp. 213**.³¹⁵ This polymer showed stable bright blue PL (Q.E. = 91 % in toluene), and showed no green emission in the annealed film (although no device preparation has been reported as yet).

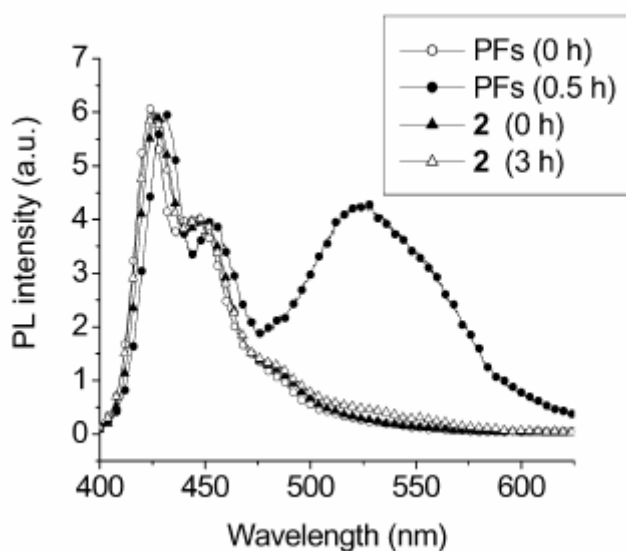
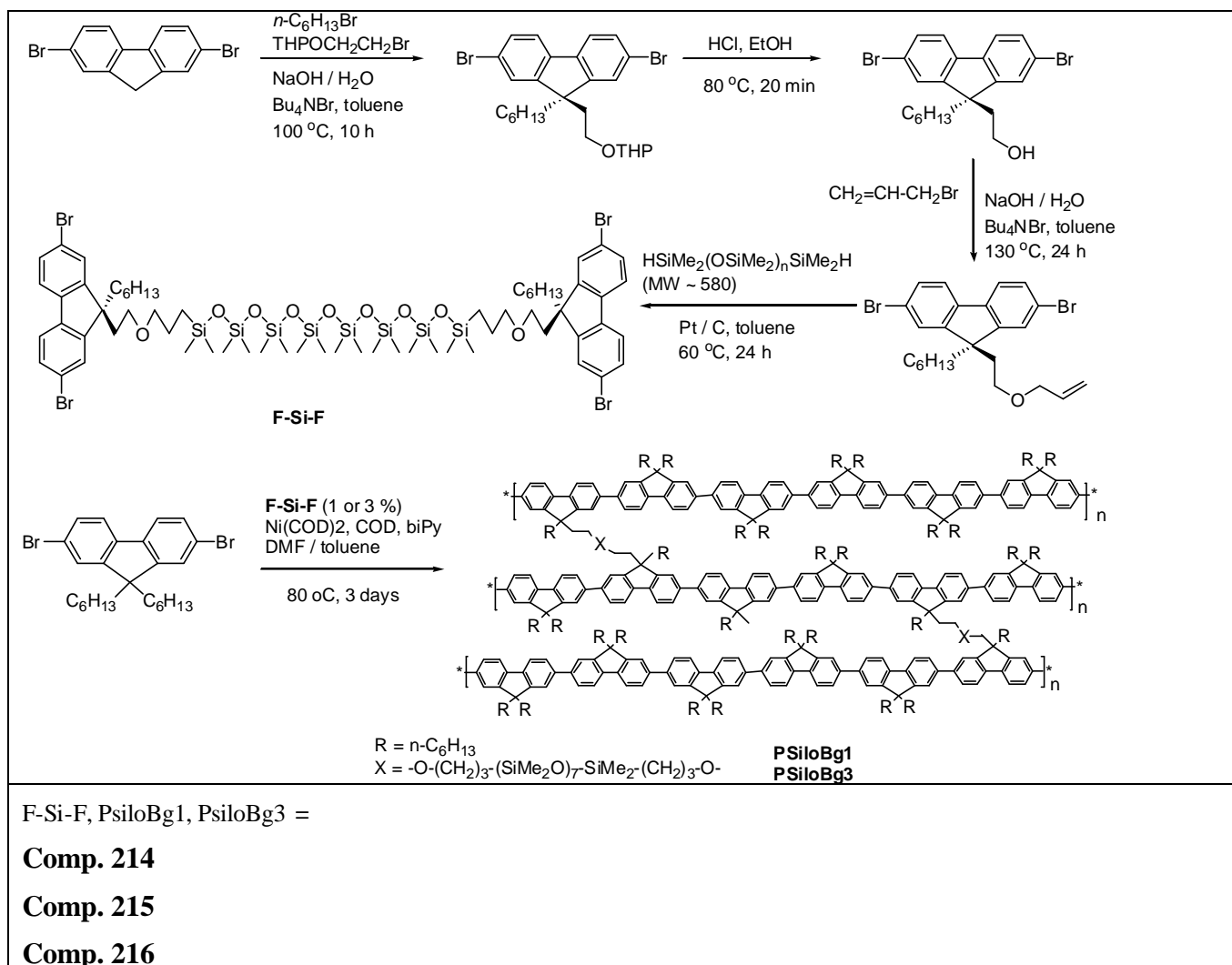


Figure 16. PL spectra of polymer **Comp. 213** and poly(dialkylfluorene) [**2** and PFs in figure, respectively] in films before and after thermal annealing at 200 °C for different times [From Ref. 315, © American Chemical Society].

Shim and co-workers synthesized cross-linked PF co-polymers containing siloxane bridges **Comp. 215** and **Comp. 216**. Ni-mediated co-polymerization of 9,9-dihexyl-2,7-dibromofluorene in the presence of 1 or 3 mol. % of bridged monomer **Comp. 214** resulted in co-polymers **Comp. 215** and **Comp. 216** in which PF backbones networked by siloxane chains (Scheme 33.).³¹⁶ Their electrochemical and spectral properties were close to that for PDHF **Comp. 187**. On the other hand, the co-polymers showed increased T_g values (106 and 110 °C, respectively) as compared to the parent PDHF **Comp. 187** and almost pure blue emission, which is stable towards annealing: whereas FWHM for **Comp. 187** after annealing of the film at 150 °C for 4 h is increased to 85 nm, **Comp. 215** and **Comp. 216** showed FWHM only 52 and 51 nm, respectively (Figure 17). Authors discussed these results in terms of hindered aggregation/excimer formation in such cross-linked PFs.



Scheme 33. Synthesis of cross-linked polyfluorenes with oligosiloxane bridge.

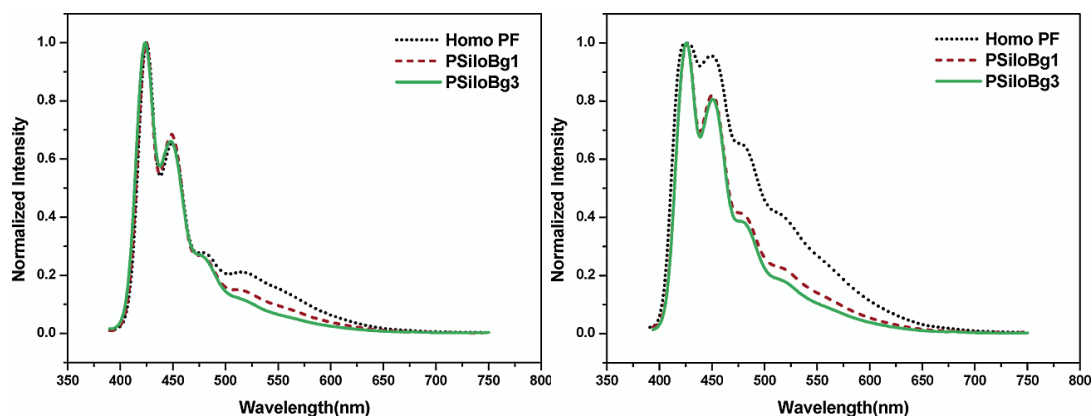
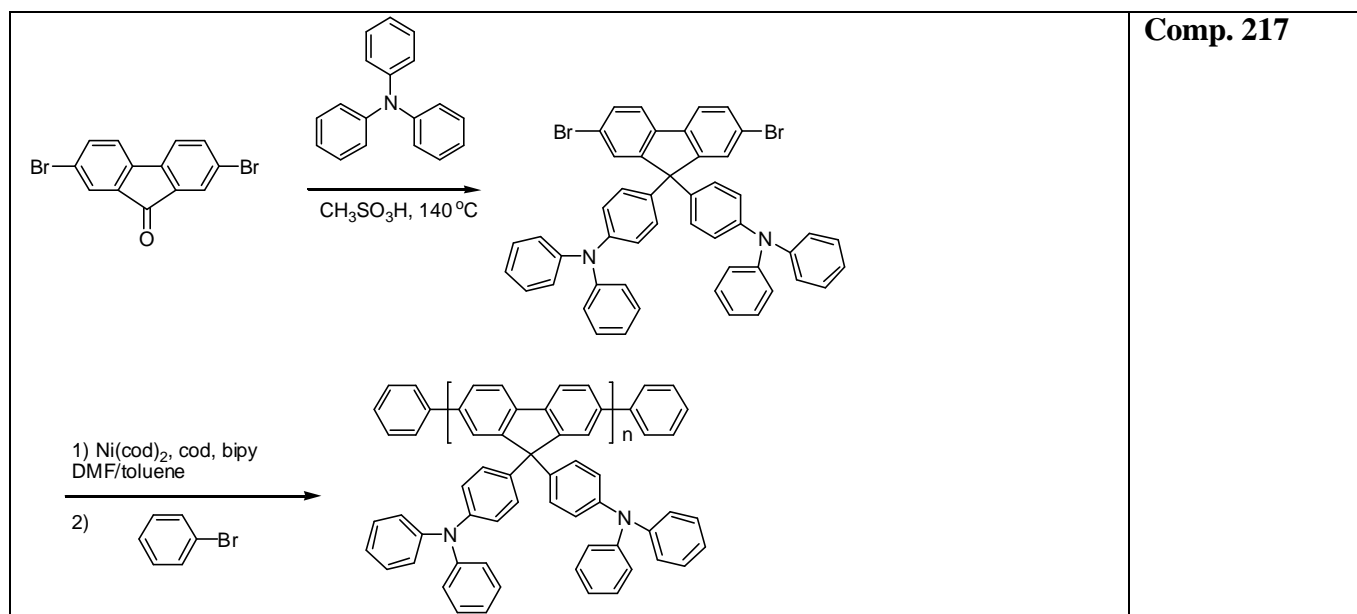


Figure 17. PL spectra of PDHF **Comp. 187** (Homo PF), **Comp. 215** (PSiloBg1) and **Comp. 216** (PSiloBg3) as spin-coated films (1500 rpm, p-xylene) and annealed at 150 °C for 30 min (left) and 4 h (right). [From Ref. 316, © 2003 American Chemical Society].

The approaches described above only dealt with structural modifications improving the processability of the polymer and suppressing the undesirable aggregation tendency of PFs. For electronic applications, and particularly LEDs, even more important is balancing the charge transport properties. For the best device performance, the transport of holes and electrons should be equalized without changing the HOMO–LUMO gap of PF (which determines the emission color). To achieve this, Scherf et al. blended the light-emitting PF with triarylamine-based hole-transport molecular compounds and demonstrated the increase of the device efficiency (up to 0.87 cd/A) and brightness (up to 800 cd/m²).³¹⁷ Furthermore, a very substantial decrease of the green emission at 520 nm in these blends was observed.

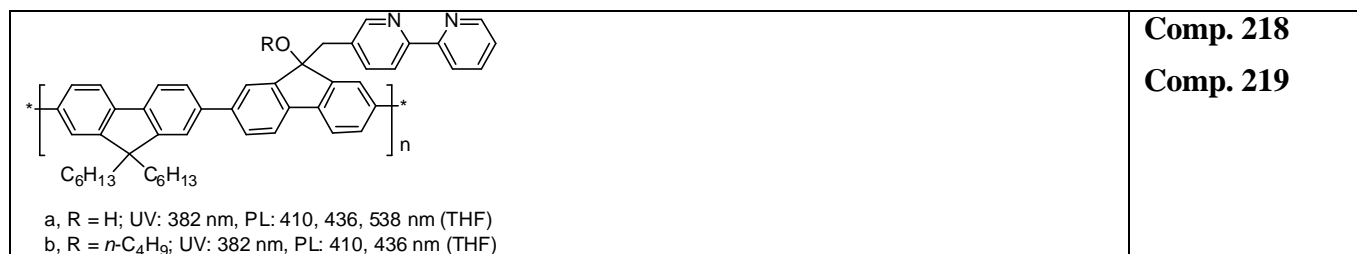
However, a phase-separation problem in the above two-component system may affect the device stability. To overcome the problem Müllen et al. introduced triphenylamine groups as side chains at the PF backbone.³¹⁸ The triphenylamine substituents simultaneously improve the hole-transport properties of PF (facilitating the injection of holes), prevent the aggregate formation, due to steric shielding effect, and bring high solubility to the material. The synthesis of such polymer, poly[9,9-bis(4-diphenylaminophenyl)-fluorene] (**Comp. 217**) included arylation of commercially available 2,7-dibromofluorenone with a large excess of triphenylamine in methanesulfonic acid and Yamamoto polymerization of the formed dibromo-monomer followed by the end group capping to give the desired polymer (Scheme 34). The obtained polymer is very soluble in common organic solvents and has the polymerization degree of *ca.* 14 unit in the chain ($M_n = 8,860$, PDI = 1.76; GPC analysis against a polyphenylene standard). The polymer emits blue light in solution and in the solid state, with a quantum efficiency of 22 % in thin films, a value half of that of dialkyl-PF (~50 % in the solid),³¹⁹ but the emission spectrum did not change after thermal annealing of the film.



Scheme 34 Synthesis of triphenylamine-substituted PF.

The triarylamine groups in **Comp. 217** improve the hole-transporting properties and reduces the diodes turn-on voltage. A single layer PLED ITO/PEDOT/**Comp. 217**/Ba starts to emit blue light (CIE: $x = 0.184$; $y = 0.159$) at as low as 4 V (1 cd/m^2) as shows the maximal current efficiency of 0.67 cd/A (0.36 lm/W). The EL spectrum shows a nearly complete suppression of the green emission. The effect can be rationalized by charge (hole) trapping effect of the triarylamine moieties, which compete with electron trapping on the fluorenone defects, and minimize the emission from the defect sites. Introducing an additional HTL (PVK) allows to further improve the device performance: maximal current efficiency of 1.05 cd/A was demonstrated by blue emitting PLED ITO/PEDOT/PVK/**Comp. 217**/Ba (CIE: $x = 0.19$, $y = 0.181$), although the maximal brightness demonstrated by both device was relatively low (up to $200\text{--}300 \text{ cd/m}^2$).

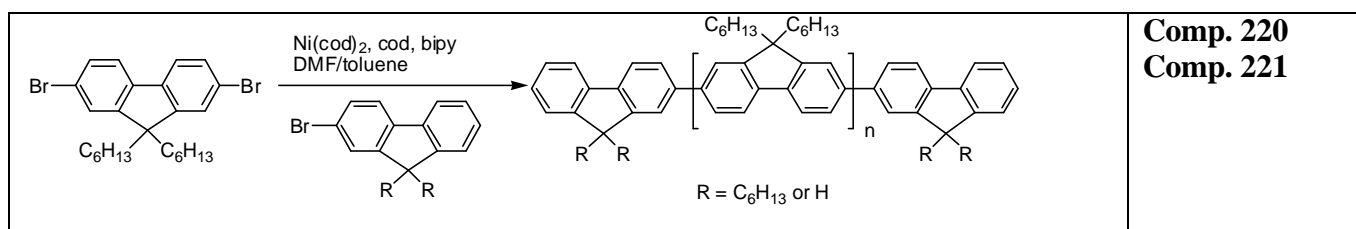
Two PFs **Comp. 218** and **Comp. 219** with 2,2'-bipyridyl side group were reported by Pei et al.³²⁰ In solution both polymers show typical PF fluorescence (410, 436 nm), but in low-polar non-hydrogen bonding solvents the hydroxy-polymer **Comp. 218** has an additional weak emission at 500–650 nm. In solid films, this low energy emission becomes dominant, which is not the case for alkylated polymer **Comp. 219**. This implies that the hydrogen bonding strengthen the intermolecular interactions in **Comp. 218**, changing the emission color from blue (in solutions) to yellow-orange (in films).



2.7. End-capped PFs

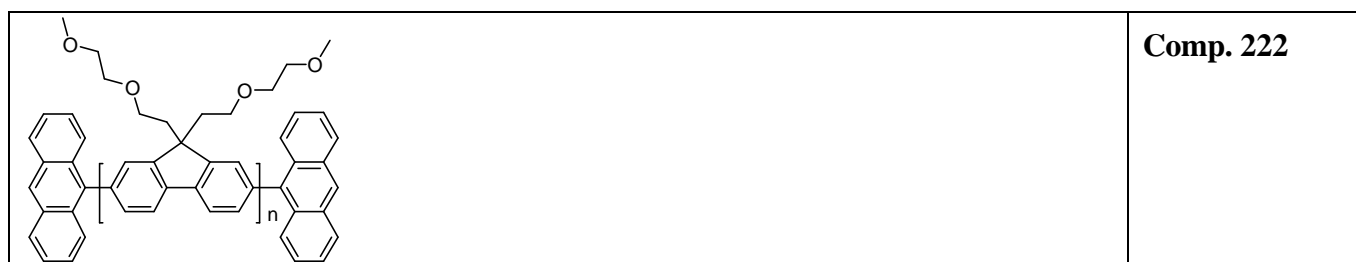
The very first and obvious reason for introducing the end groups, terminating the polymer chain was to replace reactive functionalities (halogen, boronic acid or metal-organic group), which can quench the fluorescence and/or decrease the stability of the material. Secondly, varying the feed ratio of the end-capping reagent, one can control the molecular weight of the polymer. Some examples of such utilization of end-capping approach have been demonstrated in the previous section. The third important reason for end-capping is tuning the optoelectronic properties of the polymer by electronically active end-cappers. The most important examples of functional end-capped PFs, such as the hole-transport or electron-transport groups, dye moieties and cross-linkable functionalities are given below.

The initial work introducing end-capping group in PFs was reported by IBM's group.²⁴⁵ They also systematically studied the stability of the polymers after end-capping.²⁸⁴ The end-capped polymers **Comp. 220**, **Comp. 221** have been synthesized by Yamamoto coupling polymerization (Scheme 35). Comparison of the 9-*H*-fluorene and 9,9-dihexylfluorene end-capped polymers unequivocally indicate on higher color stability of the later, which again confirms the fluorenone-based origin of the green band.



Scheme 35. Synthesis of dihexyl-PF end-capped with 2-fluorenyl groups.

Miller et al. reported using anthracene end-capper (which is twisted orthogonally in respect to the neighboring fluorene moiety) in PF **Comp. 222** to enhance the color stability of PLEDs.³²¹ However, the results show that the PLED fabricated with the anthracene end-capped polymer still suffer from the color instability (appearance of green emission band), unless the anthracene unit is also introduced as a co-monomer (at 15% level).²⁸⁴



The high efficiency PLED with excellent color stability has been fabricated with PFs **Comp. 223** and **Comp. 224**, end-capped with hole transporting triarylamine moieties.²⁴⁹ Rather high HOMO (−5.6 for **Comp. 224** and −5.48 eV **Comp. 223**) brought by triarylamine moieties facilitates the holes transport, although the authors claim that the current in devices ITO/PEDOT/polymer/Ca is still dominated by the electron transport. The best performing material (maximum luminance of 1600 cd/m² at 8.5 V and EL efficiency of 1.1 cd/A) has been achieved at the feed ratio of the end-capper (triarylamine) to the fluorene monomer of 4%. Compared with the non-endcapped polymer, the EL efficiency was increased by more than one order of magnitude, without disturbing the electronic

structure of the backbone. As in triarylamine-substituted PF **Comp. 217**, the parasitic green emission in **Comp. 223** and **Comp. 224** was completely suppressed, giving pure blue color (CIE: $x = 0.15$, $y = 0.08$) at voltages above 4 V (Figure 18). This effect can be attributed to less effective electron-hole recombination on the green-emitting species (fluorenone defects) due to competing charge trapping on the hole-transporting units. A very high EL efficiency (up to 3 cd/A) can be obtained with polymer **Comp. 223** in multistructured PLEDs, containing cross-linked HTL made of several triarylamine-based polymer layers with different HOMO levels.³²²

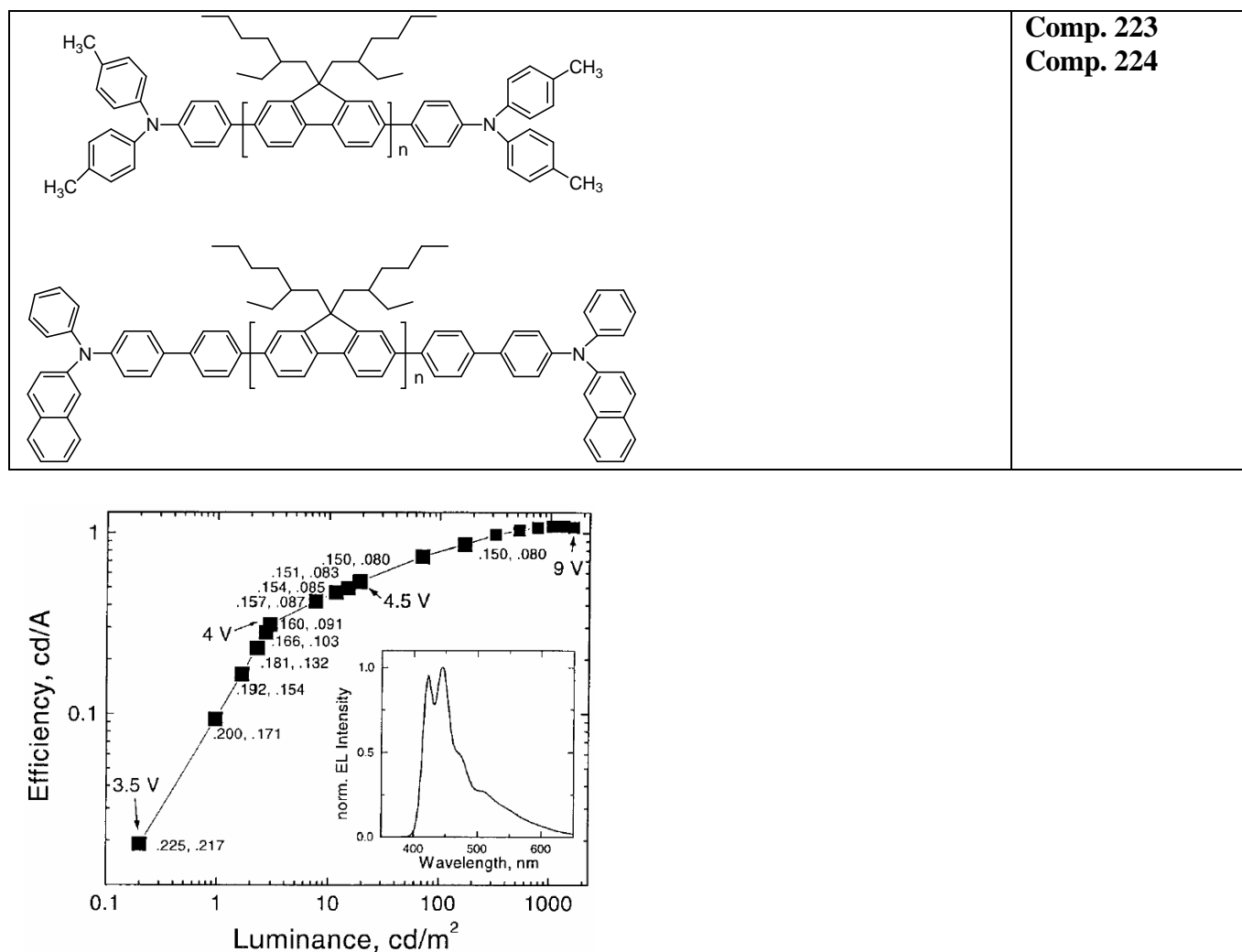
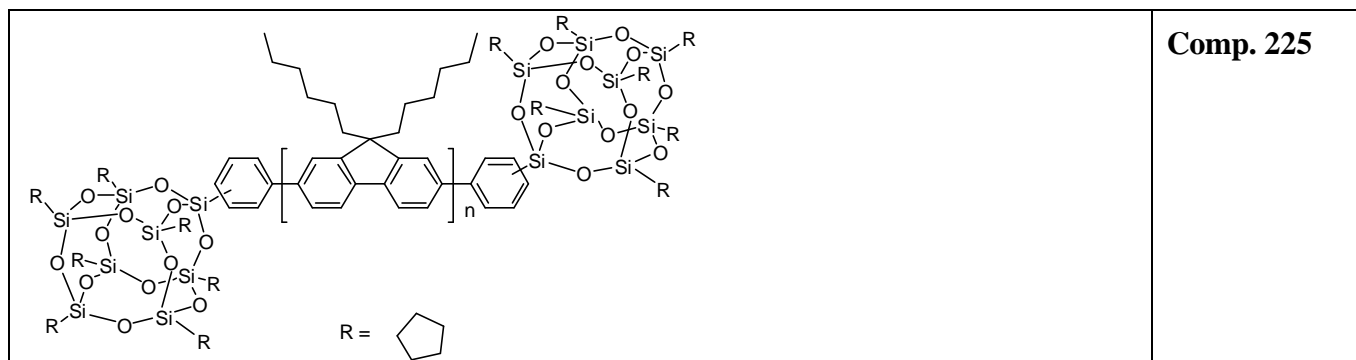


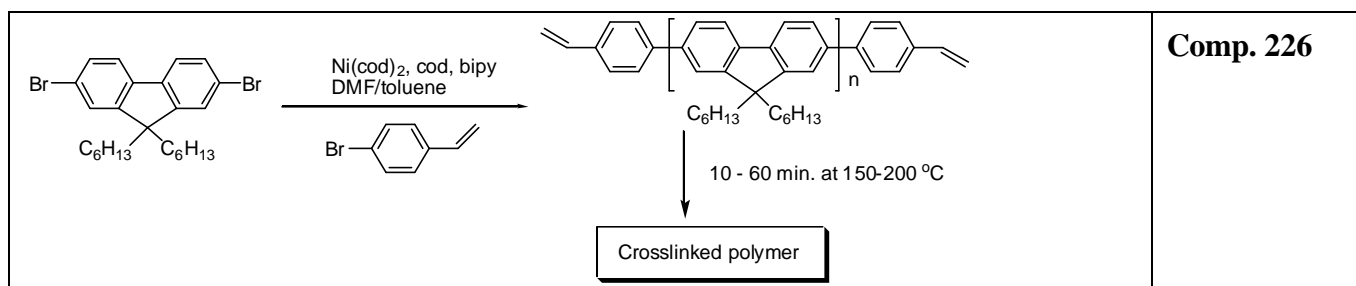
Figure 18. The efficiency-luminance plot for ITO/PEDOT/**Comp. 223**/Ca device. The numbers along the curve are the CIE coordinates at the corresponding brightness levels. The insert shows the EL emission spectrum of a diode driven at 3.6 V. [From Ref. 249, © Wiley-VCH 2001].

Very recently, Heeger's group reported PF capping with polyhedral oligomeric silsesquioxane (POSS) bulky group.³²³ The hybrid organic-inorganic polymers containing POSS segments have several advantages such as the increased thermal stability, improved adhesion between the substrate and polymer layer. The molecular weight (M_w) of **Comp. 225** (GPC vs. polystyrene) was as high as 10^5 g/mol. There is no essential difference in UV-Vis and PL between **Comp. 225** and PDHF **Comp. 187**, but the PLED devices fabricated with the former showed increased external Q.E. and somewhat

improved blue color purity (which still suffered from residual green emission). Also, the silsesquioxane end-capped PF show much higher thermal stability.



An interesting and important approach of using the end-capping styrene group for cross-linking the polyfluorene chains was reported by Miller et al. (Scheme 36).^{324,325} The cross-linking during the thermal annealing of the film renders an insoluble material, which can be used as a substrate for spin-casting the next layer in multilayer LEDs. In addition, the cross-linking drastically increases the T_g temperature, thus suppressing the formation of aggregates and giving pure blue emission.



Scheme 36 Synthesis of cross-linked PF **Comp. 226**.

The obtained polymer is completely soluble in common solvents as CHCl_3 , THF, xylene or chlorobenzene, and can be spin-cast in thin films, which are easily cross-linked upon heating (as shown by FTIR spectroscopy) to deliver an insoluble material. A relatively high amount of cross-linkable units, however, is required to completely suppress the green emission band. It was achieved by adjusting the fluorene / styrene molar ratio from 85:15 to 67:33; the later ratio delivered rather short polymer ($M_n = 3500$ g/mol, ca. 10 FI units in the chain), which upon cross-linking (200 °C, 10 min) reveals no green band in either PL and EL spectra. However, incorporating the cross-linkable units in the side chain of fluorene co-polymer (in similar ratio) does not lead to complete suppression of green emission, although it does deliver an insoluble cross-linked polymer. The last finding suggests that an improved purity of the end-capped material (due to conversion of reactive chain ends), and not the aggregation suppression due to geometric constrains of cross-linked polymer, is responsible for the pure blue emission.

Some other PFs end-capped with cross-linkable groups as benzocyclobutene have been patented by Dow Chemical.²⁷¹⁻²⁷³ For example, the thermal curing of spin-coated polymer **Comp. 227** gave an insoluble pin-hole free film without alternation of the fluorescent properties.



End-capping with hole-transporting triarylamine and electron-transporting oxadiazole moieties has been shown to tune the charge injection/transport without altering the electronic properties of the semiconducting polymer. Comparative studies of polymers **Comp. 228**, PFO **Comp. 188** and **Comp. 229** showed that the current density increased in the order **Comp. 229** < **Comp. 188** < **Comp. 228** for “hole-only” device and in the order **Comp. 228** < **Comp. 188** < **Comp. 229** for “electron-only” device (Figure 19).³²⁶ Because the hole current in the “hole-only” devices was an order of magnitude larger than the electron current in the “electron-only” devices, electron injection/transport should be more critical for the performance of a real “ambipolar” device. *[did not get this conclusion]* Devices fabricated with polymer **Comp. 229** instead of PFO **Comp. 188** demonstrated ca. 20% increase in brightness and luminance efficiency.

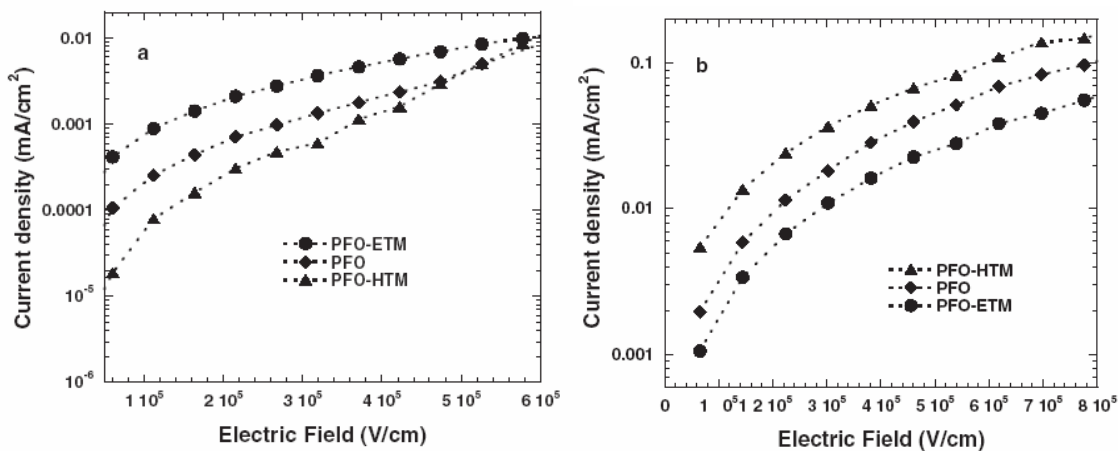
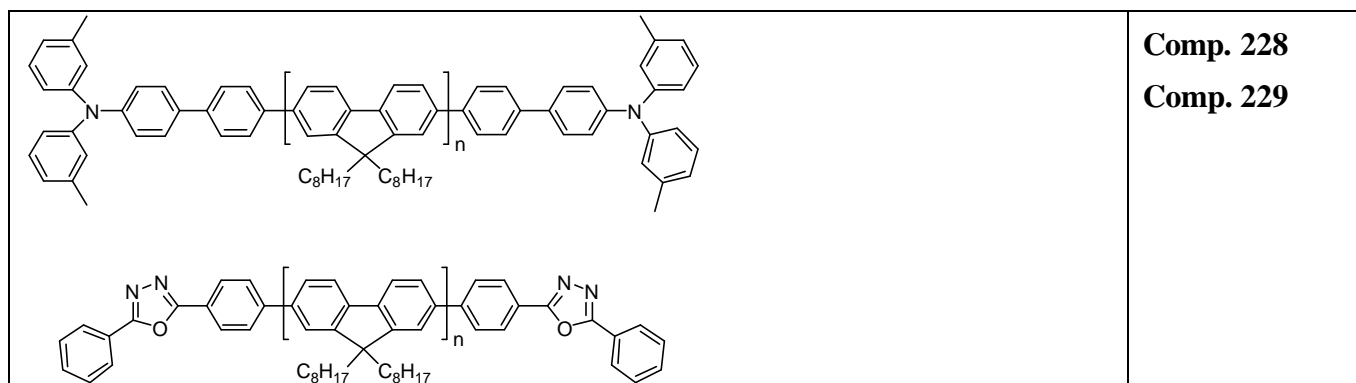
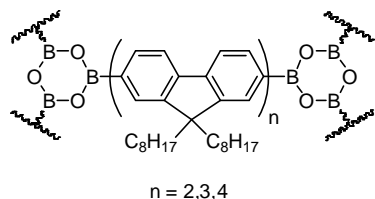


Figure 19. Current density versus electric field for PLEDs based on **Comp. 188** (PFO), **Comp. 228** (PFO-HTM) and **Comp. 229** (PFO-ETM). (a) “Electron-only” devices Yb/polymer/Ba/Al; (b) “hole-only” devices: ITO/polymer/Au [From Ref. 326, ©Wiley-VCH, 2004].

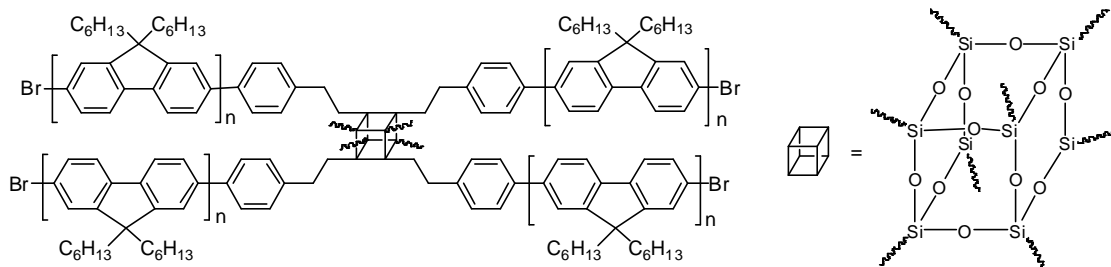
2.8. 3D Polyfluorenes

Networked materials with oligofluorene fragments were prepared by thermal treating of oligofluorene-diboronic acids.³²⁷ They exhibit high thermal (TGA: $T_{\text{dec.}} = 363\text{--}420\text{ }^{\circ}\text{C}$) and morphological (DSC: $T_g = 173\text{--}202\text{ }^{\circ}\text{C}$) stability and emit violet-blue or blue light (depending on the number of fluorene units in the fragment). The cured films exhibit almost unchanged absorption and PL spectra even after heating at $150\text{ }^{\circ}\text{C}$ for 24 h, although the performance of double layer devices ITO/CzBA/**Comp. 230**/Mg/Al (CsBA = 9-octylcarbazole, a hole-transporting material) was very poor.



Comp. 230

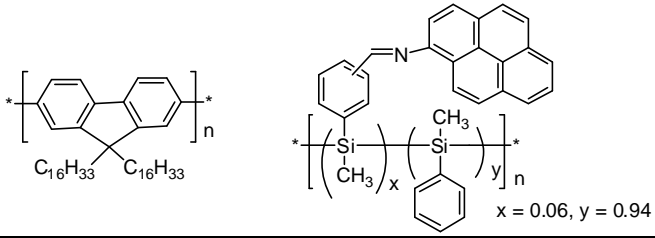
Starlike polyfluorenes **Comp. 231** with a silsesquioxane core have been prepared by Ni-mediated co-polymerization of 2,7-dibromo-9,9-dioctylfluorene with octa(2-(4-bromophenyl)ethyl)-octasilsesquioxane.³²⁸ The polymer is thermally stable up to $424\text{ }^{\circ}\text{C}$ (TGA). In both chloroform solution and films its absorption and PL spectra are very close to that for PFO **Comp. 188**, although somewhat higher PL efficiency is observed in films (64% and 55%, respectively). The polymer **Comp. 231**, however, demonstrates a better PL color stability during thermal annealing. An ITO/PEDOT/**Comp. 231**/Ca/Ag device can be turned-on at 6.0 V, and shows a brightness of $5,430\text{ cd/m}^2$ (at 8.8 V) with external Q.E. (0.44%) almost twice as high as that for the corresponded PFO device.



Comp. 231

2.9. Blends of PFs with other polymers.

It was shown that adding low oxidation potential material to PFs can stabilize the emission color and increase the device efficiency.³¹⁷ However, using low-molecular weight organic dopants cause several problems, such as phase separation and crystallization. These problems can be partially solved by using polymer blends. Cimrová reported using low ionization potential ($I_p = 5.1\text{--}5.2\text{ eV}$) aromatic polysilane **Comp. 233** as a blend polymer for poly(9,9-dihexadecylfluorene-2,7-diyl) (**Comp. 232**) ($I_p = 5.8\text{ eV}$).³²⁹

	Comp. 232 Comp. 233
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Since the ionization potential of **Comp. 233** matches closely the work function of PEDOT (5.1–5.3 eV),³³⁰ the hole injection is dramatically improved. Accordingly, the device ITO/PEDOT/**Comp. 232:Comp. 233** (7:3)/Al has a significantly improved EL efficiency $\eta_{\text{EL}} = 1.5 \text{ cd/A}$, which is two orders of magnitude higher than that of single layer PLED with **Comp. 232**, six times higher than that of bilayer PLED with triarylamine polymer HTL, and almost twice higher than that of polyfluorene blends with low-molecular triphenylamine HT materials (in device with Ca electrode).³¹⁷

Highly stable blue EL was also achieved in single layer PLEDs fabricated from the binary blends of conjugated PFO **Comp. 188** with either stable poly(vinyldiphenylquinoline) **Comp. 234** or polystyrene as demonstrated by Jenekhe's group.³³¹ PLEDs fabricated in the configuration of ITO/PEDOT/Polymer blend/Al showed the brightness and EL efficiency enhanced by a factor of 5–14 as compared to neat PFO material. Besides, the color stability was also greatly improved, particularly for **Comp. 234** blends (which possessed the highest T_g). The authors suggest that spatial confinement of the emissive excitons and improved electron-hole recombination in the “diluted” materials is responsible for the observed improvements.

	Comp. 234
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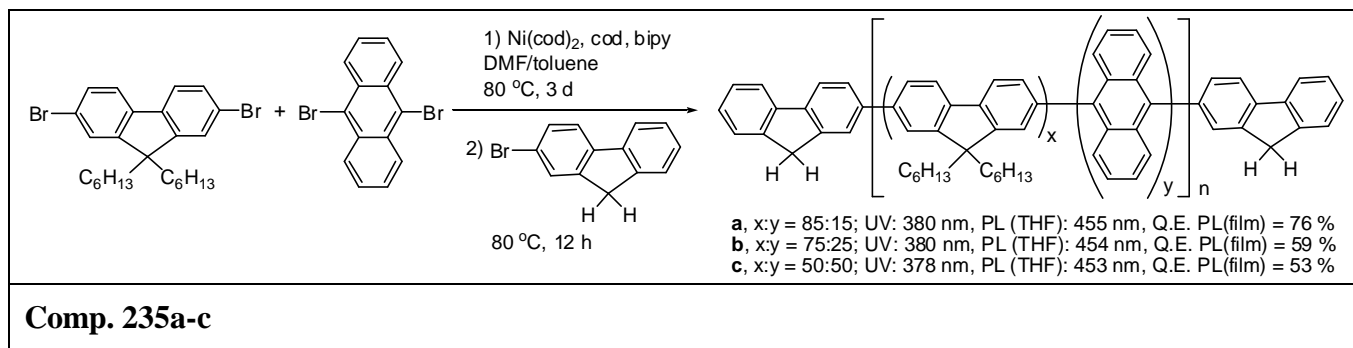
Enhanced environmental stability was recently demonstrated for PLED with PFO **Comp. 188** / gold nanoparticles (5–10 nm) nano-composite emitting layer.³³² In addition, the gold nanoparticle-doped PLEDs (1.5×10^{-5} volume fraction of Au) demonstrated improved luminescent lifetime and 2–3 times higher quantum efficiency as compared with pure PFO based PLED.

2.10. PF co-polymers

Copolymerization of fluorene with other highly luminescent materials offers a possibility of fine tuning the emitting and charge-transport properties of PF.

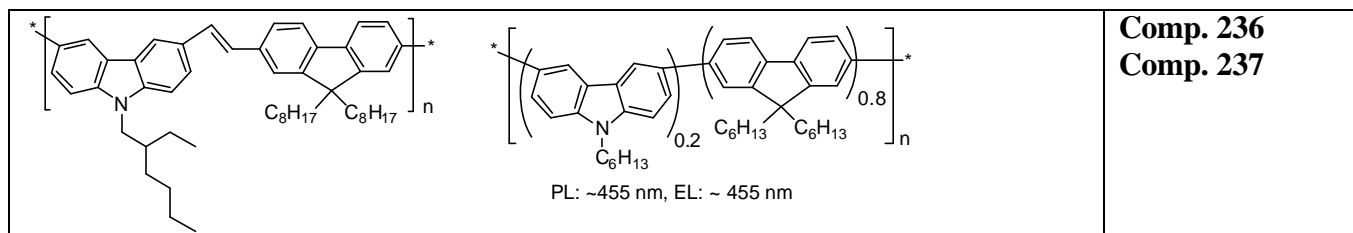
Miller et al. used nickel-mediated copolymerization to synthesize reported on random fluorene-anthracene copolymers **Comp. 235a-c**, which showed high molecular weights ($M_n = 73,000\text{--}89,000$), good thermal stability ($T_g > 400^\circ\text{C}$), high glass-transition temperatures ($T_g = 135\text{--}139^\circ\text{C}$), and high Q.E. of PL (53–76 % in films) (Scheme 37).^{333,334} Increased stability of blue emission (for **Comp. 235a** even after annealing at 200°C for 3 days), was explained in terms of preventing excimer formation due to incorporation of anthracene units, which are orthogonal to the plane of fluorenes in the backbone, although this can also be an effect of diminishing of exciton migration towards fluorenone defects. The device ITO/PANI/**Comp. 235a**/Ca/Al showed stable blue EL emission (CIE: $x = 0.17$, $y = 0.25$) with

an external Q.E. of 0.17%.³³³ Similar fluorene-anthracene copolymers with 3,6-dioxaocetyl substituents in fluorene moiety and different end-capping groups have also been reported.^{284,321}



Scheme 37. Synthesis of anthracene-fluorene copolymers.

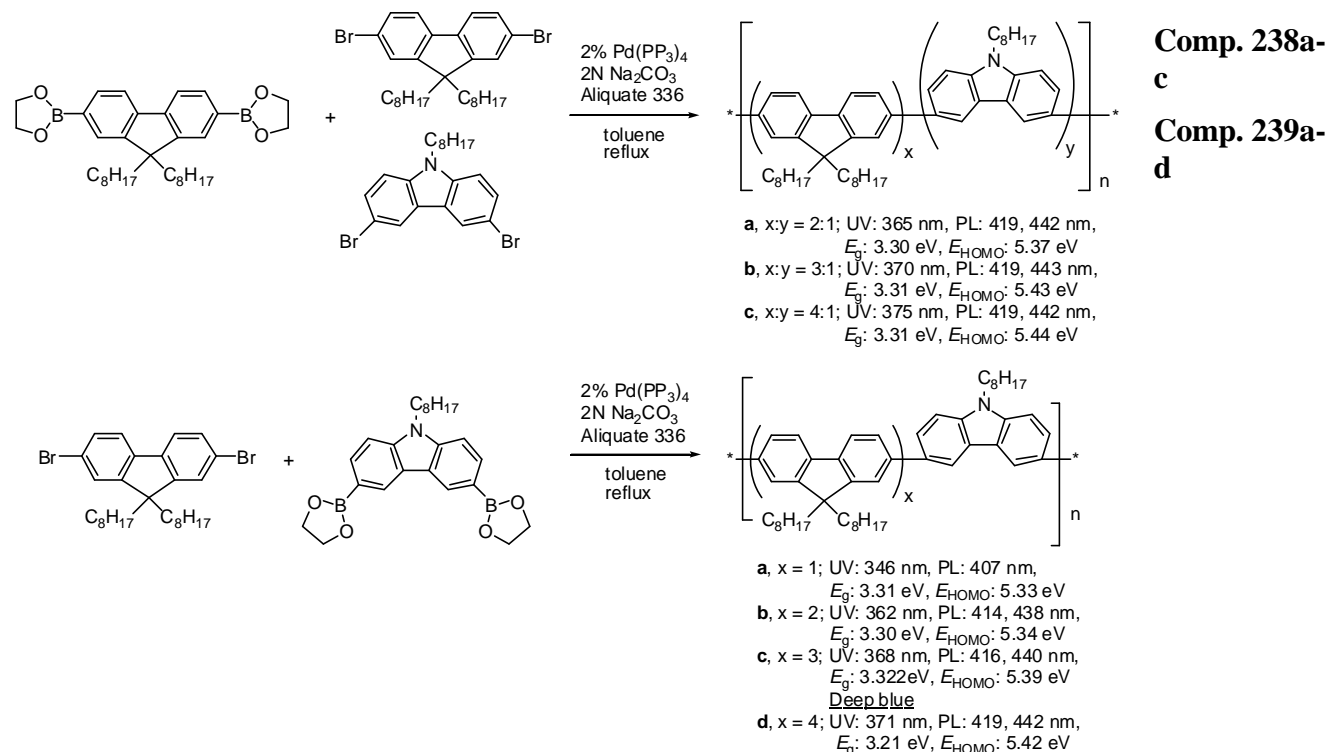
Several groups studied carbazole derivatives as co-monomers for blue-emitting PF materials. Carbazole has lower I_P (and thus lower HOMO energy level) than fluorene and many of its oligomers and polymers (e.g. well known PVK) are good hole-transporting materials. Therefore, such modification of the fluorene polymers could improve the hole transporting characteristics of PFs. Kim et al. have reported one of the first alternating fluorene-carbazole polymers **Comp. 236** synthesized by Wittig reaction of carbazole-3,6-dialdehyde with corresponded fluorene-2,7-bis(methylphosphonium) salt.³³⁵ The PLED fabricated by sandwiching a spin-coated co-polymer thin film between ITO and Al electrodes is a white emitter with FWHM of 150 nm. Blending the polymer **Comp. 236** with PVK in 4:1 ratio narrows the electroluminescence emission band ($\lambda_{\max} = 460$ nm) to give pure blue color. However, the turn-on voltage for the LED is quite high (13 V), and the external Q.E. is only 0.002%.



Later, a random co-polymer **Comp. 237** with slightly different substituents pattern was synthesized by Stéphan et al. by Ni-polymerization.³³⁶ Both co-polymers were soluble in organic solvents and had molecular weight of $M_n \sim 4,000\text{--}5,000$ g/mol (ca. 15 units). The PL spectrum of the polymer **Comp. 237** is identical to that of corresponded fluorene homopolymer, and increasing the amount of carbazole units (from 1:4 to 4:1) only results in decrease of emission intensity. The authors suggest that only oligofluorene units are responsible for the emission, and assume inhomogeneous distribution of co-monomers, with relatively long homo-oligomers sections. Low Q.E. for the polymers having high content of carbazole can be due to interruption of conjugation, brought by carbazole-3,6-diyl units (effect of the meta-substitution). *I did not see 4:1 copolymer in that paper; they stated that Carb improve hole injection, lowering turn-on voltage (nothing about low QE and other bad things...)*

The effect of regularity in fluorene/carbazole co-polymers have been very recently studied by comparison of random and alternating co-polymers **Comp. 238** and **Comp. 239**.³³⁷ Both random and alternating co-polymers showed progressive blue shifts in absorption at increasing contain of carbazole units. A similar blue shift was observed in PL for co-polymers **Comp. 239**, but all random co-polymers **Comp. 238** showed almost identical PL spectra, similar to that for PFO **Comp. 188** (UV: 387 nm, PL:

420, 442 nm / film/, E_g^{CV} : 3.25 eV, E_{HOMO} : 5.63 eV, in conditions similar for the co-polymers in **Scheme 38**). This difference between the alternating and regular co-polymers was attributed to the longer fluorene sequences (> 5 fluorene units) in random co-polymers **Comp. 238** and migration of the excitons to these segments where the emission occurs. The device ITO/**Comp. 239c**/F-TBB/Alq3/LiF/Al with F-TBB (1,3,5-tris(4'-fluorobiphenyl-4-yl)benzene) as hole-blocking layer showed maximum luminance of 350 cd/m² at 27 V, and luminance efficiency of 0.72 cd/A at a practical brightness of 100 cd/m², which is *ca.* double of that for the device with **Comp. 188** in the same conditions (160 cd/m² and 0.30 cd/A).^{337,338} Pure deep blue EL with narrow FWHM (39–52 nm) and negligible low-energy emission bands was observed for this device.³³⁸



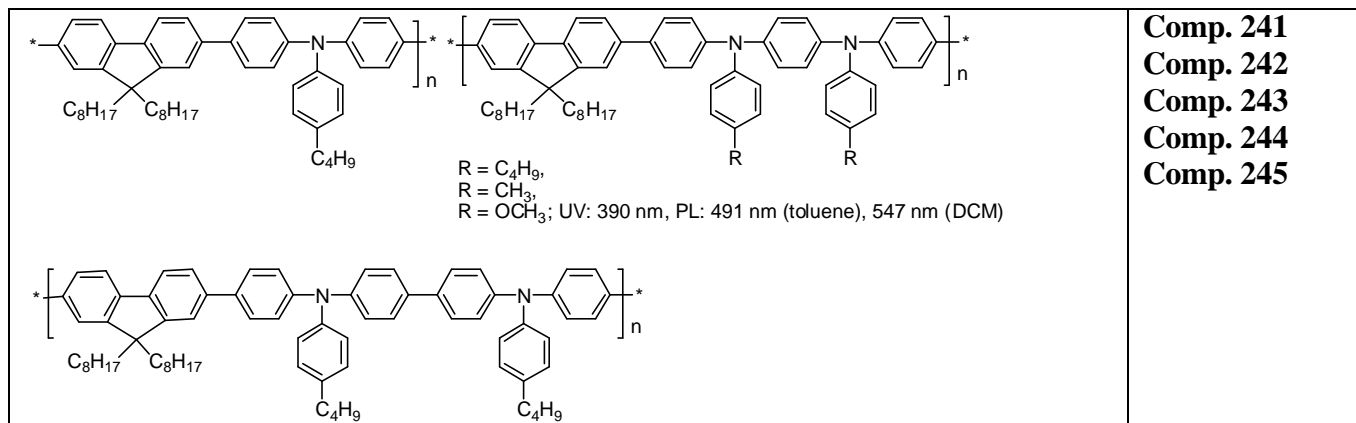
Scheme 38. Synthesis of random and alternating fluorene/carbazole co-polymers.³³⁷

Leclerc's group in Canada first synthesized PF co-polymer **Comp. 240** based on carbazole-2,7-diyl unit which is, in contrast to above examples, a fully conjugated system.^{339,340} Just as in carbazole-3,6-diyl co-polymers, **Comp. 240** showed the absorption and photoluminescent spectra similar to those of PFO **Comp. 188**, with almost the same photoluminescent Q.E. However, there was no sign of the green emission band in this co-polymer after thermal annealing.

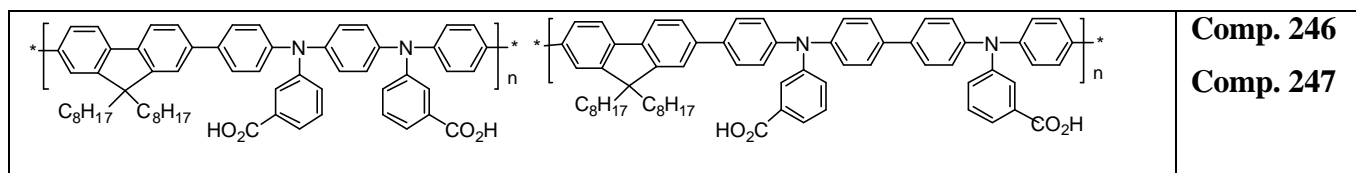


Copolymerization of fluorene with triarylamine compounds was shown to increase the hole transport properties of the polymers. Several co-polymers of triarylamine and fluorene (**Comp. 241–Comp. 245**) synthesized by Suzuki coupling were reported by Bradley et al.^{341,342} The hole's mobility

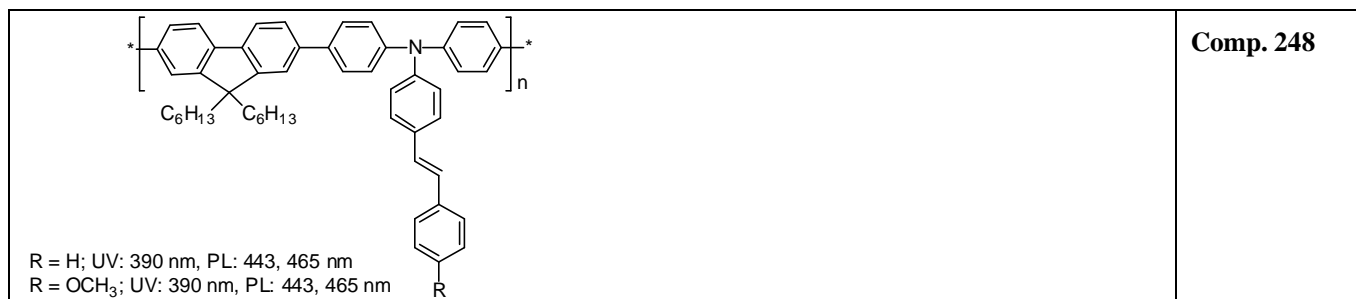
of the co-polymers was in the range of $3 \times 10^{-4} \text{ cm}^2/\text{Vs}$ to $3 \times 10^{-3} \text{ cm}^2/\text{Vs}$, and the I_p was as low as 5.0–5.3 eV (*cf.* 5.8 eV for PFO **Comp. 188**), which is in good match with workfunction of ITO/PEDOT electrode. Unfortunately, no PL or EL properties have been reported in the paper, although the PLED devices based on the blends of these co-polymers with other PF have been patented by Dow Chemical.³⁴³



Inbasekaran et al. synthesized similar triarylamine–fluorene co-polymers **Comp. 246** and **Comp. 247** possessing carboxylic acid substituents, via hydrolysis of corresponded ethyl ester polymer, prepared by Suzuki polymerization reaction.^{344,272} Due to the very polar substituents, the co-polymers **Comp. 246** and **Comp. 247** are only soluble in polar solvents such as DMF, but not in aromatic hydrocarbons as toluene or xylene, which allows simple fabrication of multilayer PLEDs by all-solution process.



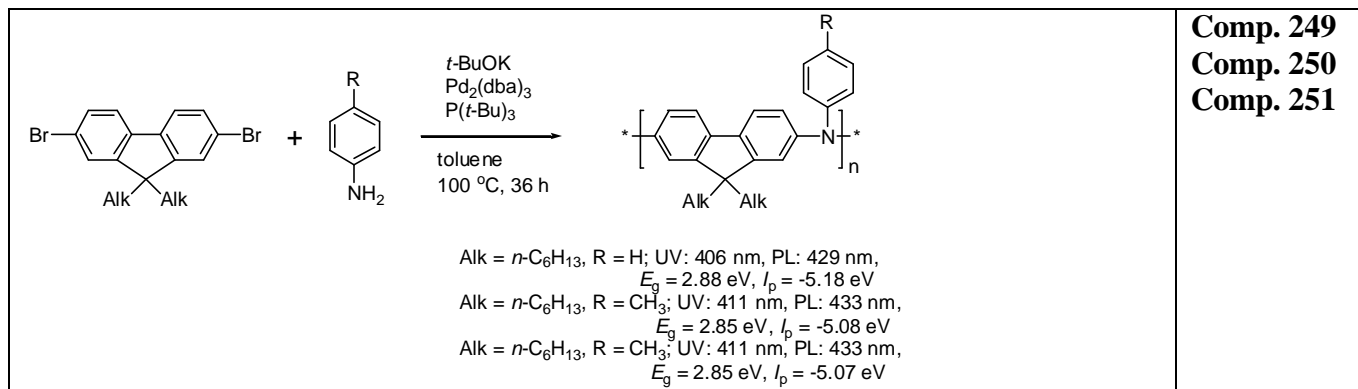
Fang and Yamamoto reported triarylamine-fluorene copolymers **Comp. 248** with stilbene pendant groups.³⁴⁵ Whereas in the solid state absorption and PL maxima of both polymers are essentially the same, PL in solution strongly influenced by the kind of solvent (from 433 nm in toluene to 466 nm in N-methylpyrrolidone). Copolymer **Comp. 248** ($R = \text{H}$) showed PLQY in the solid state of 51 %, comparable to that of poly(9,9-dialkylfluorenes).



Molecular triarylamine-based hole-transporting materials are usually synthesized by Ulmann coupling or Pd-catalyzed amination, although the polymerization using these reactions is difficult.

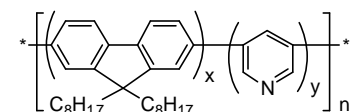
Shim et al. reported on successful Pd-catalyzed co-polymerization of dibromofluorene derivative with anilines and obtained thermally stable, reasonable high molecular weight ($M_n = 12,300 - 14,000$, PDI = 2.4 – 3.0) co-polymers **Comp. 249–Comp. 251** (Scheme 39.).³⁴⁶ The HOMO levels of these co-polymers (ca. -5.1 eV) matched well with the ITO anode. The LEDs consisting of these polymers as buffer layer demonstrated a lower turn-on voltage, enhanced efficiency and higher maximum luminance due to improved hole injection. For comparison, the devices ITO/**Comp.**

249/TPD/Alq₃/LiF/Al and ITO/TPD/Alq₃/LiF/Al showed, respectively, the turn-on voltage of 2.2 and 3.6 V, the maximum luminance (at the highest current density) of 12,370 cd/m² (at 472mA/cm²) and 5,790 cd/m² (at 233mA/cm²).



Scheme 39. Synthesis of fluorene-arylamine electron-rich co-polymers.

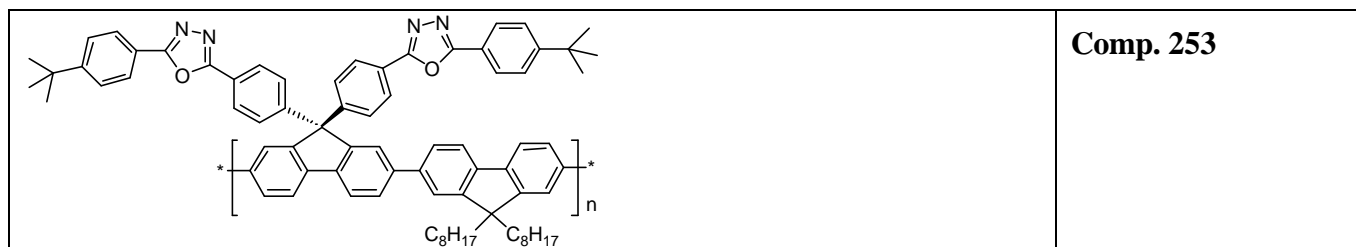
A series of random fluorene/pyridine co-polymers **Comp. 252a-f** have been prepared by Suzuki coupling of fluorene monomers when certain amount of 3,5-dibromopyridine (5, 10, 20, 30, 40, 50 mol%) has been added to the reaction mixture.³⁴⁷ Meta-linkage of the pyridine unit should interrupt the conjugation, but no regular spectral dependence was observed for different loading of pyridine co-monomer. PL spectra for all co-polymers are very close, except for co-polymer **Comp. 252f** (50:50 ratio), for which the PL and EL spectra are shifted by ~10–20 nm as compared to other co-polymers. This could be a result of longer fluorene sequences in the random co-polymers as discussed above for the fluorene/carbazole and fluorene/phenoazine co-polymers. All materials (except **Comp. 252f**) showed narrow, pure blue EL emission, and the devices in configuration ITO/PEDOT/**Comp. 252a-e**/Ba/Al had a turn-on voltage of 5–6 V, and moderately high external Q.E. of 0.4–0.5 %.



Comp. 252

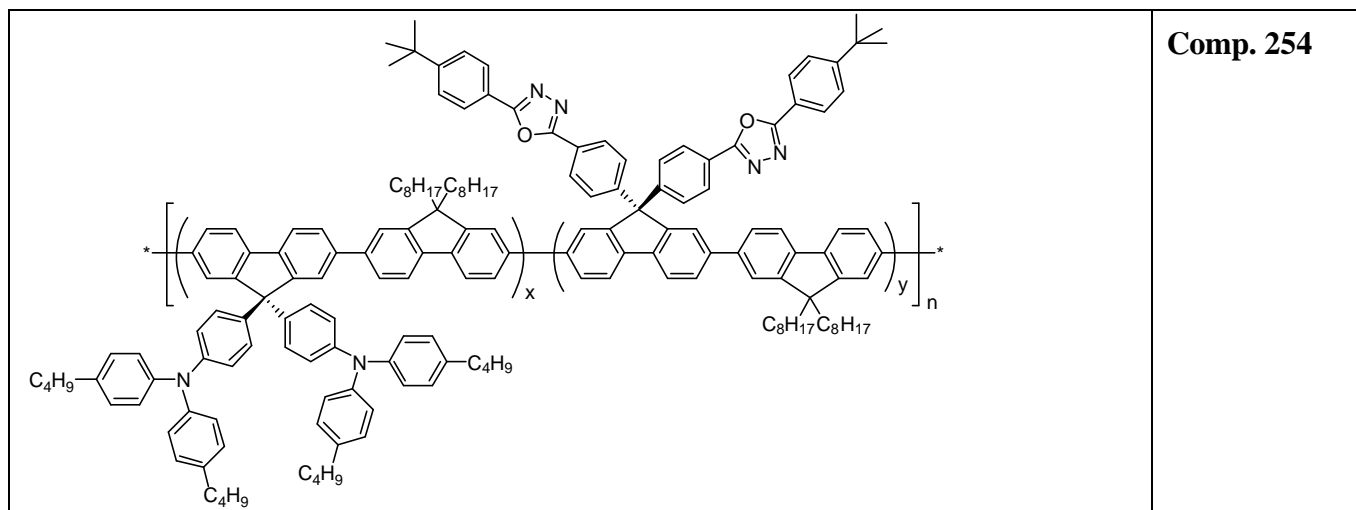
a, x:y = 95:5; UV: 380 nm, PL: 422 nm, EL: 446 nm
b, x:y = 90:10; UV: 383 nm, PL: 422 nm, EL: 442 nm
c, x:y = 80:20; UV: 380 nm, PL: 422 nm, EL: 442 nm
d, x:y = 70:30; UV: 370 nm, PL: 420 nm, EL: 438 nm
e, x:y = 60:40; UV: 380 nm, PL: 419 nm, EL: 440 nm
f, x:y = 50:50; UV: 350 nm, PL: 413 nm, EL: 424 nm

The tuning of electron injection/transport in PF has been undertaken by Shu's group, who introduced electron-deficient oxadiazole units as a pendant groups in the fluorene co-polymer **Comp. 253**.³⁴⁸ The introduction of oxadiazole units into the PF can potentially improve the electron transport properties of the polymer, and also their bulkiness can help to suppress the aggregation effects.



Comp. 253 was readily soluble in common organic solvents such as THF, chloroform, chlorobenzene and xylene. GPC analysis (vs. polystyrene standard) gave a molecular weight M_n of 13,000 g/mol, with a PDI of 2.1. The polymer possesses excellent thermal stability with a very high T_g of 213 °C. The electrochemically determined HOMO/LUMO levels of **Comp. 253** were -5.76 eV and -2.47 eV, respectively, which are similar to those of PFO **Comp. 188** (-5.8 eV and -2.6 eV), with only slightly improved electron affinity. The absorption spectrum of **Comp. 253** in THF solution showed two major peaks at 297 nm and 390 nm. The former peak is attributed to the aromatic oxadiazole group and the latter to the π - π^* transition of the polymer backbone. There is essentially no influence of the attached oxadiazole group on the conjugated backbone: the PL spectrum displays a blue emission with two sharp peaks at 419 nm and 444 nm, and a small shoulder at 469 nm, very similar to that of PFO **Comp. 188**. The PL Q.E. in solution was very high (124% vs. 9,10-diphenylanthracene as a standard; for the later, an absolute fluorescence efficiency of 90% was reported), which dropped in thin film to a value of 43%, comparable to PFO (55%). Under thermal annealing of thin films at 150 °C for 20 h, the PL spectrum of **Comp. 253** remains almost intact with only negligible long wavelength tail, which resulted in very pure blue emission color in PLED devices (fabricated as ITO/PEDOT/**Comp. 253**/Ca/Ag). The device showed a low turn-on voltage of 5.3 V, and the luminance reaches 2,770 cd/m² at 10.8 V with a current density of 1.12 A/cm². The maximum external quantum efficiency was 0.52 % at 537 cd/m² at 7.4 V. The device efficiency is much higher than that of a similar PFO-based device (maximum brightness of 600 cd/m² and external Q.E. of 0.2 %).

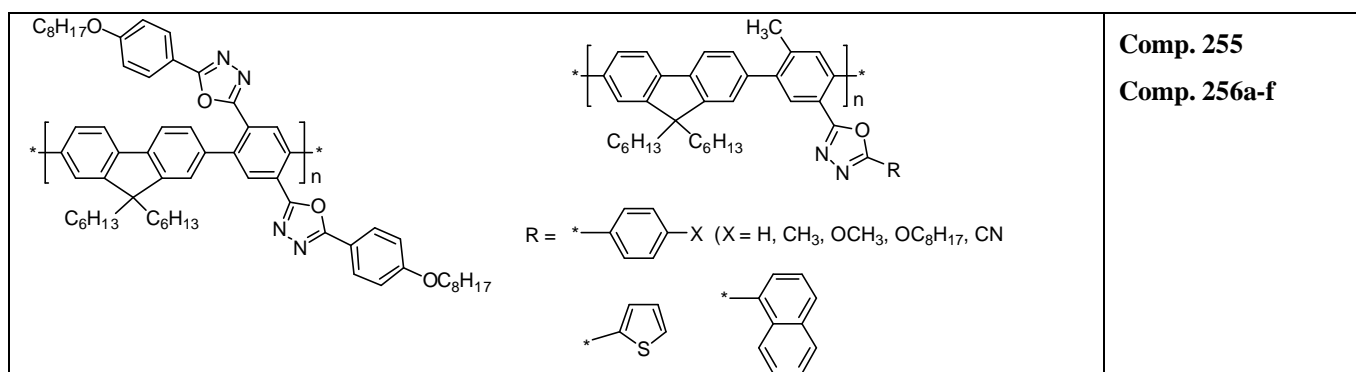
A recent paper reported a highly efficient blue color emission polyfluorene co-polymer **Comp. 254** incorporating both triphenylamine and oxadiazole pendant groups.³⁴⁹



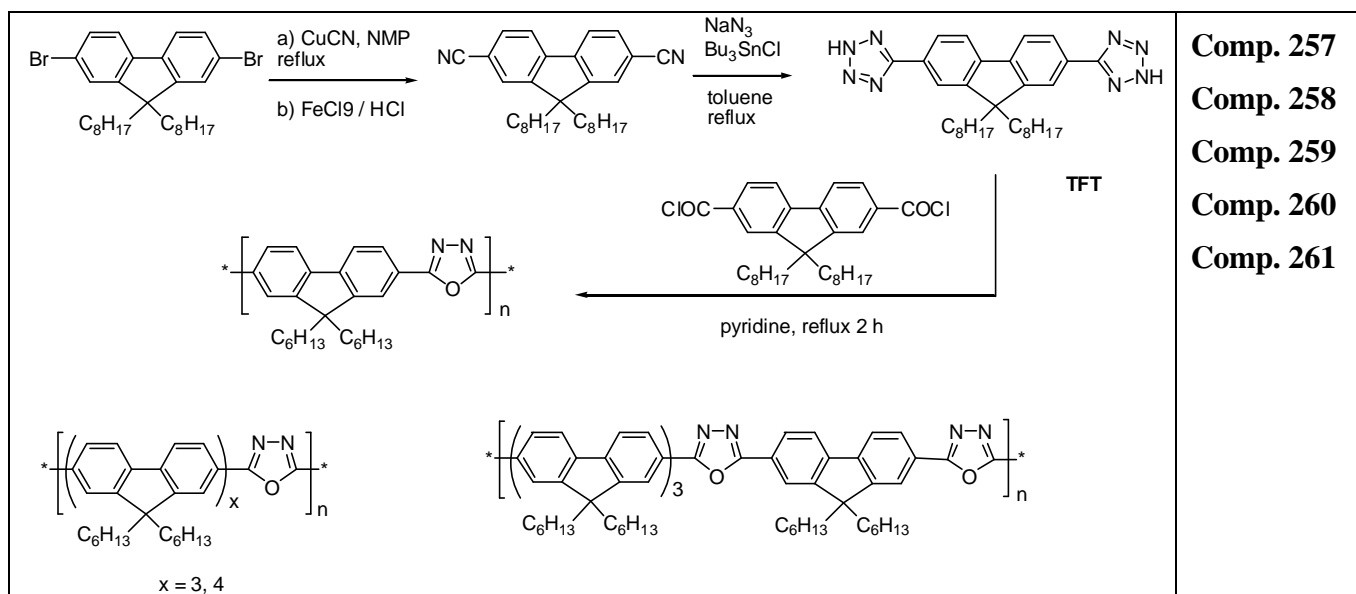
This statistical co-polymer was designed to bring together good hole transporting (due to triphenylamine groups) and electron transporting properties (due to oxadiazole groups). The co-polymer showed high solubility in organic solvents, good stability ($T_{dec} = 440$ °C, $T_g = 166$ °C) and high PL quantum efficiency (95% in solution and 42% in films) with stable emission color (unchanged

after the thermal annealing). The introduced electron-rich and electron-deficient substituents endow rather high HOMO of (−5.30 eV) and relatively low LUMO (−2.54 eV) energy levels, which should facilitate the charge injection and transport in the polymer. Indeed, the PLED device fabricated with the configuration of ITO/PEDOT/**Comp. 254**/Ca/Ag showed a low turn on voltage of 4.4 V and the maximum external Q.E. of 1.21 % (achieved at the driving voltage of 7.6 V, brightness of 354 cd/m²), which is more than twice higher than that for PF **Comp. 253** containing only electron deficient oxadiazole substituents.³⁴⁸ In spite of minor additional emission bands at 580 and 660 nm (which increase at higher voltages), this PLED emission fall into blue region (CIE: $x = 0.193$, $y = 0.141$), which, together with high maximum luminance of 4,080 cd/m² and efficiency of 0.63 cd/A (0.19 lm/W), render **Comp. 254** as a promising LEP.

A series of fluorene copolymers **Comp. 255** and **Comp. 256a-f** with oxadiazole pendant groups was recently synthesized by Sung and Lin.³⁵⁰ The EL maximum for copolymer **Comp. 255** (452 nm) is red-shifted as compared to **Comp. 256a-f** (406–431 nm). The devices fabricated with these copolymers in ITO/PEDOT/polymer/Ca/Al configuration showed relatively high turn-on voltage of 6.5–8.5 V and moderate maximum brightness (29–462 cd/m²).

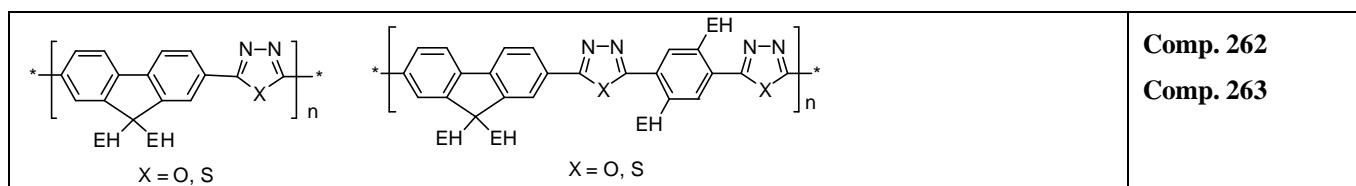


Oxadiazole unit was also introduced into the backbone of fluorene alternating co-polymers. The key monomer in synthesis of a series of fluorene-oxadiazole co-polymers was 2,7-bis(tetrazolyl)fluorene derivative **Comp. 257**, based on which co-polymers **Comp. 258–Comp. 261** were prepared.³⁵¹

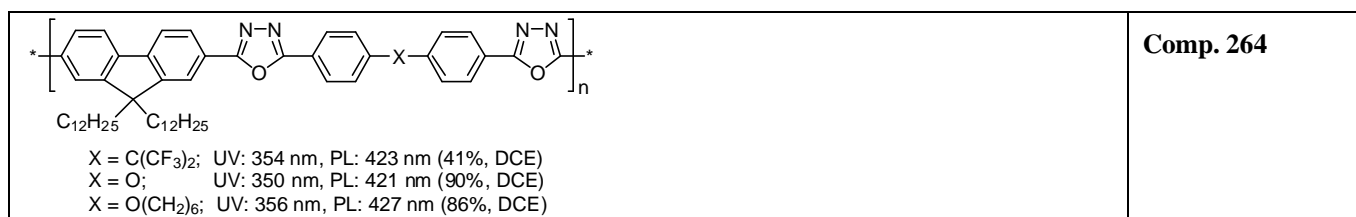


Scheme 40. Synthesis of fluorene/oxadiazole co-polymers

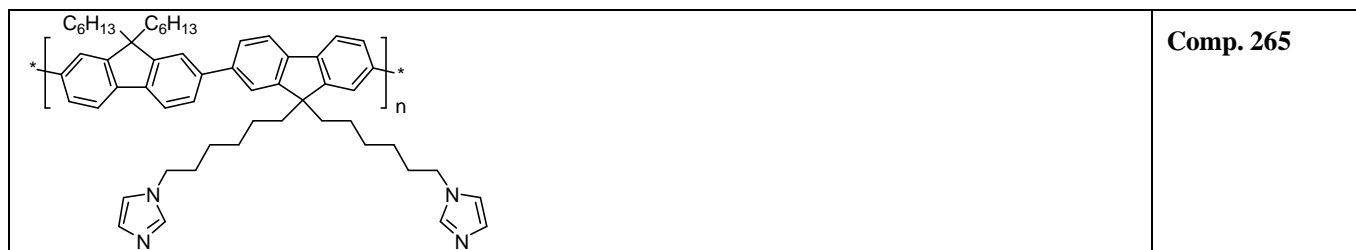
This tetrazole route has several advantages over other oxadiazole ring formation reactions: fast and clean reaction, mild reaction conditions, high yields and high molecular weights of the co-polymers. The co-polymers showed excellent thermal stability ($T_{\text{dec}} > 430\text{ }^{\circ}\text{C}$) and their glass transition temperature progressively increased from 98 to 150 $^{\circ}\text{C}$ with increasing the oxadiazole content in the polymer. Remarkably, the UV and PL spectra of the co-polymers were all very similar to those of fluorene homopolymers with only slight red shifts in absorption (10–12 nm) and emission (5–7 nm) spectra. The co-polymers also demonstrated high $\Phi_{\text{PL}} \approx 70\%$ (in DCM solution) typical for PFs. Several other fluorene-oxadiazole and fluorene-thiadiazole fully conjugated copolymers **Comp. 262**, **Comp. 263** have been prepared in the same way.³⁵²



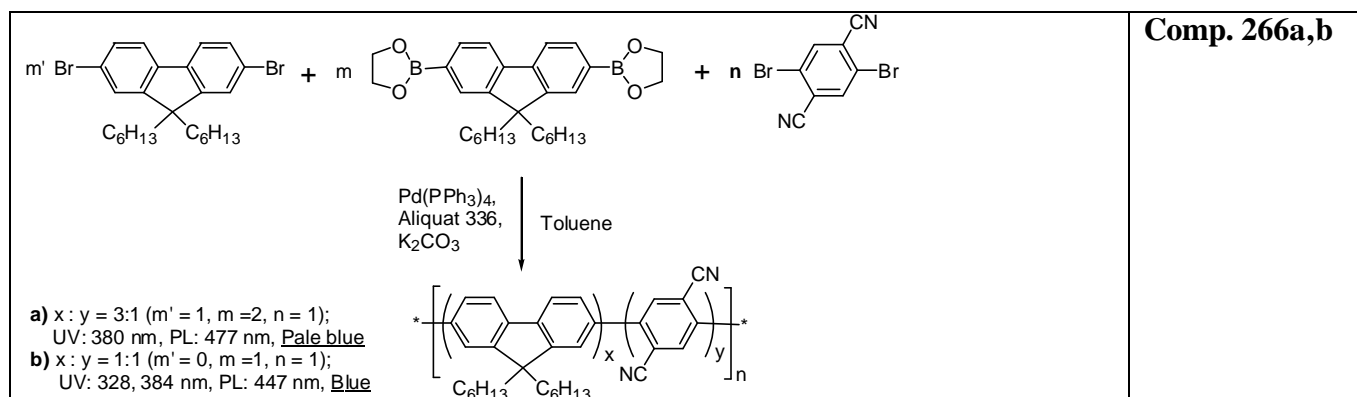
Fluorene-oxadiazole copolymers **Comp. 264** with σ -bridge in the backbone have also been reported.³⁵³ These showed significant blue shift in PL spectra due to interrupted conjugation.



Pei et al. synthesized fluorene copolymer functionalized with imidazole ligands in the side chains (**Comp. 265**).³⁵⁴ The PL emission of **Comp. 265** was sensitive to the presence of metal cations in the solution (particularly efficient quenching was due to Cu²⁺), which makes it a promising material for fluorescent chemosensing.

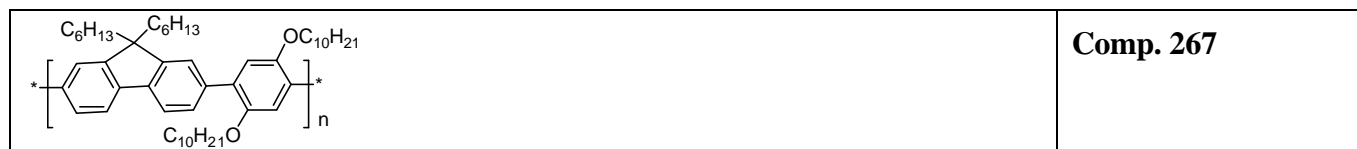


Efficient blue emission and good electron affinity and electron-transporting properties were demonstrated for two fluorene co-polymers with dicyanobenzene moiety in the main chain, **Comp. 266a,b** (Scheme 41).³⁵⁵ Due to improved electron transport properties, the device ITO/PEDOT/Comp. 266a/Ca showed a low turn-on voltage (3.4 V), better external Q.E. (0.5 %) and high brightness (5,430 cd/m²) as compared to the PDHF **Comp. 187** device in the same configuration.

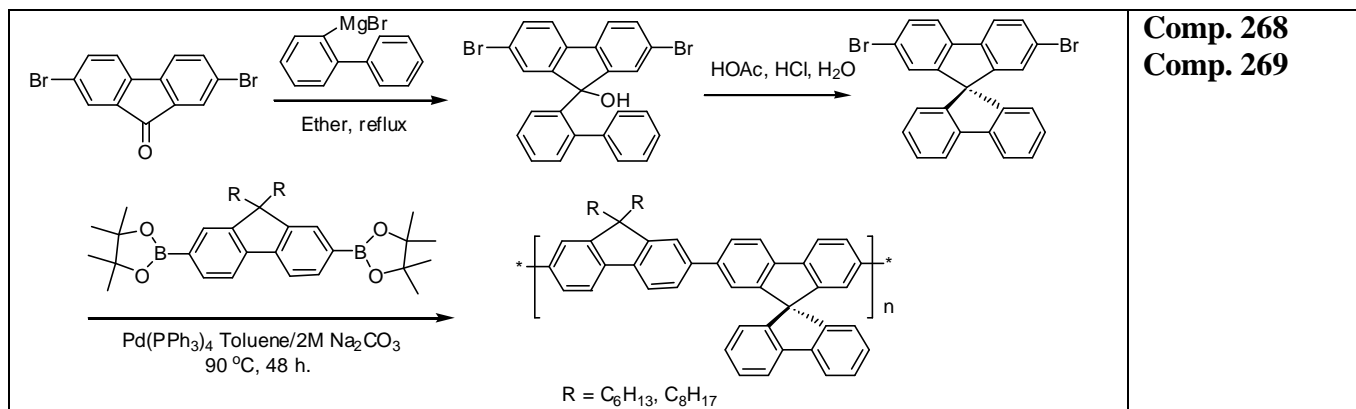


Scheme 41. Synthesis of fluorene–(2,5-dicyanobenzene) co-polymers via Suzuki coupling.

Many other PF co-polymers, which do not contain a particularly electron-active moiety, but nevertheless, can improve the performance of the material in PLED have been synthesized. The Huang's group at IMRE (Singapore) synthesized deep blue co-polymer **Comp. 267** by Suzuki co-polymerization of fluorenediboronic acid with dibromobenzene.³⁵⁶ The emission band of **Comp. 267** has two peaks at 420 nm and 448 nm with a FWHM of 69 nm, and virtually no green emission was observed, allowing for very pure blue fluorescence, as compared to PDHF **Comp. 187**. The PL Q.E. of thin films was around 40 %, which is similar to that of PDHF. The single layer PLED device (ITO/**Comp. 267**/Ca) and the multi-layer devices (ITO/PANI/PVK/**Comp. 267**/Ca and ITO/CuPc/PVK/**Comp. 267**/Ca) gave identical deep blue EL emission ($I_{\text{max}} = 420$ nm, FWHM = 53 nm).³⁵⁶ The maximum external Q.E. of 0.6 % and the maximum luminance of 700 cd/m² were achieved for a multilayer PLED.



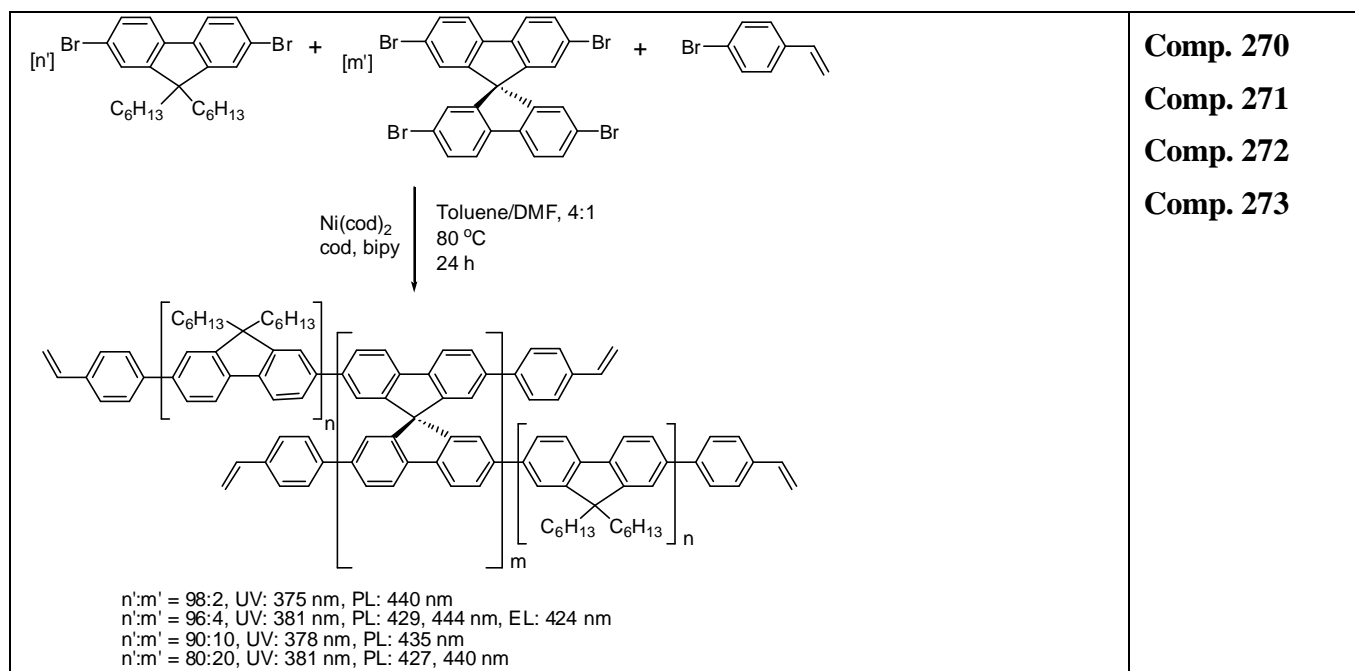
Spiro-bifluorene moiety was used to construct alternating co-polymers **Comp. 268** and **Comp. 269** with dialkylfluorene units. The aim of this modification was to increase the glass-transition temperature of the material, so as the moderate heating during the device operation would not result in aggregate formation.³⁵⁷ A 90° geometry of spiro-annulated bifluorene units prevents the interchain aggregation in the polymer, whereas the long alkyl substituents in the second co-monomer improve the solubility. The synthesis is given in the Scheme 42. Grignard reaction of 2,7-dibromo-9-fluorenone with biphenyl-2-magnesium bromide, followed by the acid promoted cyclization affords the spiro-annulated monomer. The co-polymers were synthesized by Suzuki-coupling reaction with commercially available (from Aldrich) dialkylfluorenediboronic esters.



Scheme 42 Synthesis of the PF spiro-co-polymers.

The co-polymers **Comp. 268**, **Comp. 269** are only partially soluble in solvents as THF and chloroform, but can be completely dissolved in chlorobenzene (used to spin-cast the polymer films). The M_n , determined for the THF-soluble part of **Comp. 269** is 11,600 g/mol, PDI = 2.9, although higher molecular weight is expected for the THF-insoluble part. The DSC-determined T_g of **Comp. 268** (105 °C) is higher than that of PDHF **Comp. 187** (75 °C). Consequently, no long wavelength emission was found for films annealed at 100 °C (in contrast to PDHF), although further annealing at 150 °C (i.e., above the T_g) does result in appearance of the strong emission band at 525 nm. Another feature of such co-polymers is their narrow emission spectra as compared to dialkylfluorene homopolymers, which was attributed to less dense molecular packing: for **Comp. 269** and **Comp. 187** FWHM = 39 nm and 62 nm, $\lambda_{onset}^{PL} = 585$ and 610 nm, respectively.²⁸⁷ The PLED device fabricated as ITO/**Comp. 269**/Ca gave pure blue emission with a maximum external Q.E. of 0.12 %. Adding copper phthalocyanine (CuPc) as an HTL between the ITO and co-polymer layers decreased the operating voltage from 16 V to 7 V and increased the Q.E. to 0.54 % (maximal luminance 24 cd/m²).

Random co-polymers **Comp. 270–Comp. 273** containing spiro-fluorene moiety were also reported by Carter et al. at IBM Almaden Research Center. They used spiro-bifluorene dibrominated at both fluorene moieties. Ni(0)-Mediated random co-polymerization of 9,9-dihexyl-2,7-dibromofluorene with this spiro-bifluorene monomer resulted in 3D branched co-polymers **Comp. 270–Comp. 273** (Scheme 43).³⁵⁸ Due to expected low solubility for such networked materials at high degree of polymerization, the molecular weight was controlled at $M_n \approx 3,800$ –12,800 by adding 4-bromostyrene as a terminating agent. The later also serves as a cross-linkable unit, which allows to obtain an insoluble polymer film by heating of the spin-coated (non-cross-linked) polymer. The resulting amorphous polymers **Comp. 270–Comp. 273** demonstrated excellent thermal stability ($T_{dec} > 430$ °C) and their T_g values (105, 144, 93 and 90 °C for **Comp. 270–Comp. 273**, respectively) are substantially higher than those of PDHF **Comp. 187** (75 °C). PL measurements in films reveal blue emission, which remains stable (no green component) after thermal treatment at 120 °C for 30 min (in these conditions the co-polymers are cross-linked through the 4-phenylethenyl end groups rendering the insoluble film) (Figure 20). The bilayer device ITO/PEDOT/x-HTPA/**Comp. 270**/Ca/Al was fabricated by spin-coating the cross-linkable poly(4-hexyl-triphenyl)amine (x-HTPA) as HTL, curing at 100 °C for 1 h in a glovebox, and repeating the process with **Comp. 270**. The diode could be switched on at 3 V to emit blue light ($\lambda_{EL} = 424$ nm; CIE: $x = 0.168$, $y = 0.07$) and maximum external Q.E. of 0.08 % was achieved at 9 V.



Scheme 43. Synthesis of random PFs with spiro-fluorene moieties.

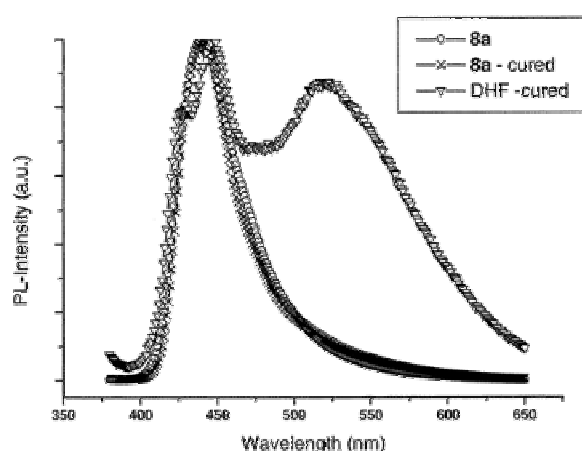
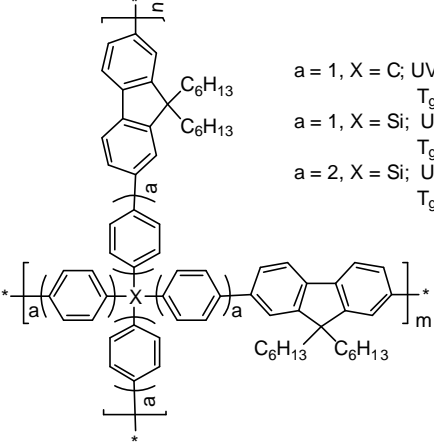


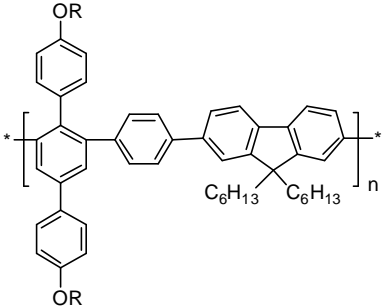
Figure 20. PL spectra of the uncured and cured amorphous spiro-PF **Comp. 270 (8a)** and a cured PDHF **Comp. 187 (DHF)**. [From Ref. 358, © 2001 American Chemical Society].

He et al. synthesized a series of hyperbranched alternating copolymers of tetraphenyl(p-biphenyl)-methane and -silane) with 9,9-dihexylfluorene by Suzuki coupling (**Comp. 274**).³⁵⁹ Remarkably, copolymers **Comp. 274** were soluble in common solvents, showed high glass transition temperatures ($> 200^\circ\text{C}$) and emitted in the blue region, slightly blue-shifted as compared to poly(9,9-dialkylfluorenes). Due to their 3D structure preventing close packing of fluorene chains, copolymers are less prone to self-aggregation in the solid state and, accordingly no green emission was observed. A PLED ITO/PEDOT/polymer/LiF/Ca/Ag showed bright blue emission peaking at 415 nm with an external Q.E. of 0.6 % and a turn-on voltage of 6.0 V.

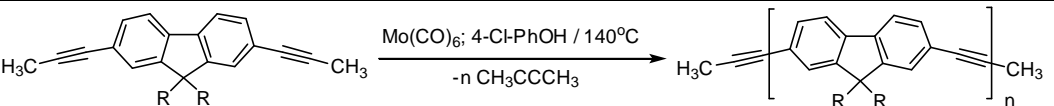
 <p> $a = 1, X = C$; UV: 345nm, PL: 399, 420sh nm, PLQY: 38%, T_g: 236 °C, T_d: 449 °C $a = 1, X = Si$; UV: 333nm, PL: 402, 419sh nm, PLQY: 65%, T_g: 237 °C, T_d: 439 °C $a = 2, X = Si$; UV: 374nm, PL: 414, 439sh nm, PLQY: 82%, T_g: 238 °C, T_d: 380 °C </p>	<p>Comp. 274</p>
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Blue light-emitting copolymers **Comp. 275** with interrupted conjugation due to meta-phenyl linkage in the backbone showed no typical for PFs vibronic structure in their PL spectra. They possess an increased stability toward appearance of undesired green emission on annealing.

ITO/PEDOT/**Comp. 275**/Ba/Al devices demonstrated turn-on voltages of 7.4–8.4 V and external Q.E. in the range of 0.43–0.6%.³⁶⁰

 <p> $R = C_6H_{13}$; UV: 341 nm, PL: 411 nm, PLQY: 32 %, EL: 418 nm $R = 2\text{-ethylhexyl}$, UV: 341 nm, PL: 408 nm, PLQY: 30 %, EL: 419 nm $R = C_{12}H_{23}$; UV: 344 nm, PL: 412 nm, PLQY: 32 %, EL: 420 nm </p>	<p>Comp. 275</p>
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An unusual synthetic approach to PF co-polymers was demonstrated by Bunz et al. who prepared poly(fluorene ethynylene)s **Comp. 276** by metathesis polymerization reaction (Scheme 44).³⁶¹ The aggregation of polymers **Comp. 276** in concentrated solutions and in solid state is manifested in slight (up to 10–20 nm) red shift of the absorbance and emission peaks for, although both the solutions and films emit pure blue light.

	<p>Comp. 276</p>
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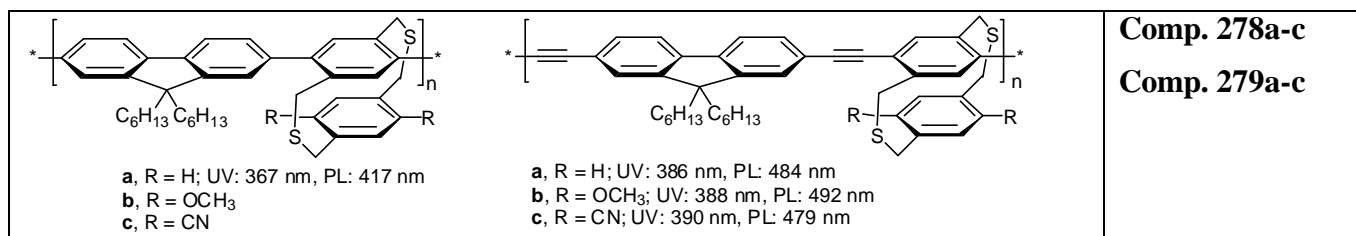
Scheme 44. Metathesis polymerization synthesis of fluorene-ethynyl co-polymer **Comp. 276**.

Jen et al. reported a binaphthyl-containing random PF co-polymer **Comp. 277**, synthesized by Suzuki coupling reaction.³⁶² The twisted binaphthyl units control the effective conjugation length, and prevent the quenching of the fluorescence in the solid state by hindering the intermolecular π - π interactions. Accordingly, a pure blue emission (two peaks at 428 nm and 448 nm, blue-shifted

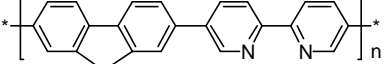
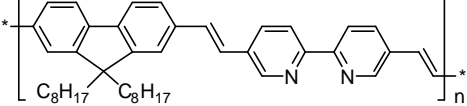
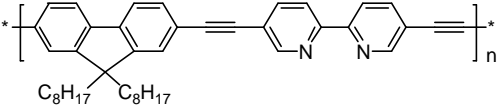
comparing to PFO **Comp. 188**) and a relatively high PL efficiency (44 %) was observed in solid films of this material. Multilayer PLEDs fabricated with copper phthalocyanine or BTPD-PFCB (**Comp. 130**³⁶³) HTL (ITO/HTL/**Comp. 277**/Ca configuration) exhibited EL emission peaks at 420 nm and 446 nm with EL maximum brightness and external Q.E. of up to 3,070 cd/m² and 0.82 %, respectively (although an additional low intensity emission band was observed for the most efficient devices using BTPD-PFCB as an HTL).^{362,363}



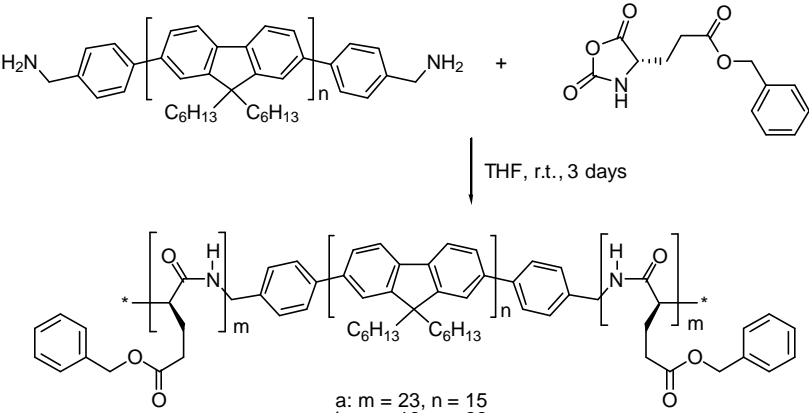
Recently, Lai et al. reported fluorene co-polymers, containing dithia[3.3]cyclophane as a repeating unit.^{364,365} The polymers **Comp. 278** and **Comp. 279** were synthesized by Suzuki coupling fluorene borate compound with dibromocyclophane. The polymer **Comp. 278a** shows pure blue fluorescence with rather high PL quantum yield (75%), but no LED device performance was reported. Remarkably, introduction of any (electron donor or electron acceptor) substituents in the cyclophane moiety results in significant quenching of the fluorescence quantum yield (36% for **Comp. 278b**, 0% for **Comp. 278c**), which was explained by trans-annular charge transfer effect.³⁶⁴ Co-polymers **Comp. 279a-c** also showed lowering in quantum yields (15–22%).³⁶⁵



Huang et al. reported alternating fluorene co-polymers **Comp. 280–Comp. 282** containing 2,2-bipyridyl fragment in the main chain using Suzuki, Wittig-Horner and Heck coupling of 9,9-dioctyl-2,7-dibromofluorene, respectively.³⁶⁶ All three polymers were responsive to a wide variety of transition metal ions by an absorption spectral red shift (up to 40 nm) and fluorescence quenching.

 <p>UV: 383 nm, PL: 453, 477 (425) nm</p>	Comp. 280 Comp. 281 Comp. 282
 <p>UV: 432 (459) nm, PL: 521 nm</p>	
 <p>UV: 425 (395) nm, PL: 477, 503 (439) nm</p>	

Kong and Jenekhe prepared triblock copolymers **Comp. 283** by the ring-opening polymerization of γ -benzyl-L-glutamate *N*-carboxyanhydride using benzylamine-end-capped poly(9,9-dihexylfluorene) (**Scheme 45**).³⁶⁷ The polymers retain the emissive properties of PF ($\lambda_{\text{abs}}^{\text{max}} = 380$ nm, $\lambda_{\text{PL}}^{\text{max}} = 424$ nm in CHCl_3) and show EL with a brightness comparable to PF homopolymers. Different nanostructured assemblies of the block copolymers **Comp. 283** were observed by AFM depending on the copolymer composition and the secondary structure (helix or coil) of the polypeptide blocks.

 <p>a: $m = 23, n = 15$ b: $m = 16, n = 28$</p>	Comp. 283
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Scheme 45. Synthesis of triblock copolymers Comp. 283.

2.11. Color Tuning in PFs co-polymers

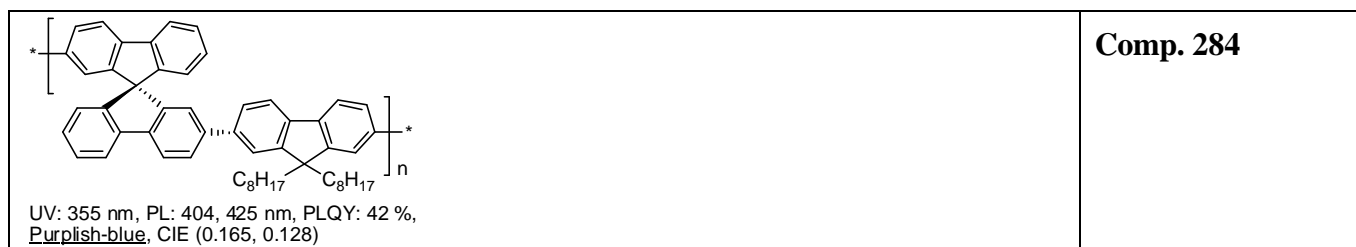
The above strategies were focused on creating highly stable PFs with pure blue emission. However, other emission color can be also achieved through doping with fluorescent dyes or through co-polymerization strategy in either alternating or random PF co-polymers. Through careful selection of suitable co-monomers, considering their effect on HOMO/LUMO levels of the polymer, one can achieve a whole range of emission colors from PF-based materials.

2.11.1 Doping with low-molecular fluorescent dyes

The high energy blue emission of PF polymers can be changed into virtually any color by adding small amount of low-energy emitting materials. This approach, based on energy transfer is of prime importance for phosphorescent PLEDs (see Chapter 7), although non-phosphorescent dyes have also been used to tune the PF emission color. Thus, efficient Förster energy transfer from blue to red (typical for porphyrines) color was demonstrated for tetraphenylporphyrine (TPP)-doped PFO **Comp. 188** based LED as a result of the good overlap between the PF emission with the Soret absorption band of the porphyrine.³⁶⁸ It was shown that for composites with 1–10 % of TPP, 95 % of photogenerated excitons are transferred from the polymer to TPP. The ITO/**Comp. 247**/**Comp. 188**:TPP/Ca LED (**Comp. 247** here plays the role of HTL) showed external EL Q.E. of 0.9 % at 33 V, corresponding to 0.18 cd/A and a luminance of 90 cd/m². The EL emission was identical to the PL emission of TPP, with CIE coordinates ($x = 0.65$, $y = 0.29$) representing a rather pure red color.

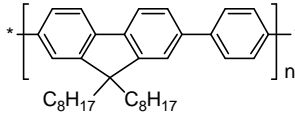
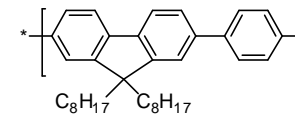
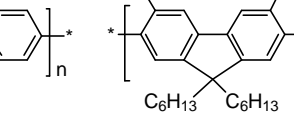
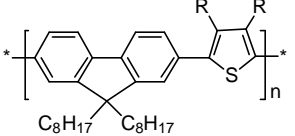
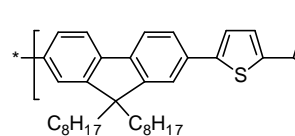
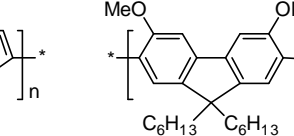
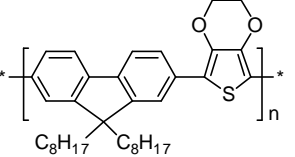
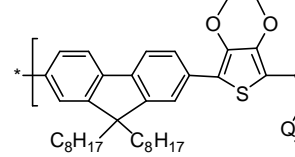
2.11.2 Alternating co-polymers

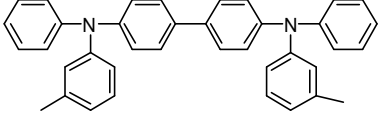
Wu et al. has recently reported a new spiro-linked polyfluorene (**Comp. 284**).³⁶⁹



Unlike the spiro-*co*-PF discussed in the previous section, the conjugation in **Comp. 284** is completely interrupted by the spiro-bifluorene units. As a result, the co-polymer showed a significant blue shifted absorption and emission spectra, compared with PFO **Comp. 188**. The UV-Vis absorption of thin films coated from a toluene solution has a maximum at 355 nm and the PL emission showed a vibronic fine structure with two sharp peaks at 400 nm and 422 nm. The quantum efficiency of the polymer in thin films is 42 %, comparable to PFO. This co-polymer shows superb color stability: the thermal annealing of thin films has no effect on the emission. While the co-polymer itself demonstrates a purple-blue emission on the UV limit of the visible region of spectra (CIE: $x = 0.165$, $y = 0.128$), it can be used as an energy transfer material with fluorescent dyes to achieve a desirable color. Thus, the pure blue emission is easily achieved with ca. 1% of 2,5,8,11-tetra-*tert*-butylperylene dye.

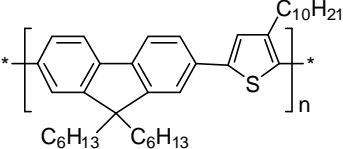
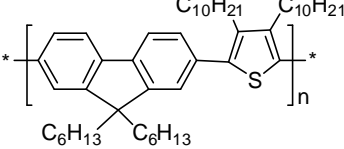
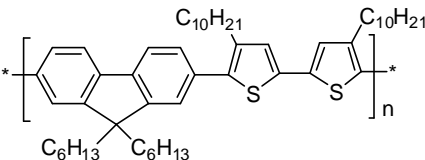
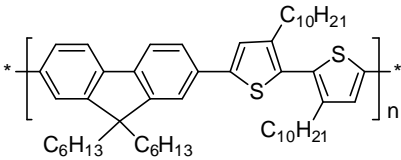
Lévesque and Leclerc have efficiently tuned the emission color from blue to green and yellow by introducing various phenylene and thiophene units in alternating fluorene co-polymers **Comp. 285–Comp. 291**, although no simple correlation between the polymer structure and the EL color has been found^{299,370,371} Changing the nature of the co-monomer unit from the relatively electron-deficient phenylene to very electron-rich bis(ethylenedioxy)thiophene affects the band-gap of the polymer (and, thus, the emitting color) and the charge-transport properties, thus influencing the performance of the PLEDs based on corresponded co-polymers (see also ref. 372 on thermo and solvatochromic properties of these copolymers). The highest brightness achieved for bithiophene-based co-polymer **Comp. 289** was of 4.5 cd/m² for a neat co-polymer and 18 cd/m² for a blend with 20% of hole transport material TPD (**Comp. 293**), which is far too low for a practical application.

			Comp. 285 Comp. 286 Comp. 287 Comp. 288a,b Comp. 289 Comp. 290 Comp. 291 Comp. 292
UV: 364 nm, PL: 420, 442 nm EL: 419 nm, <u>Blue violet</u>	UV: 365 nm, PL: 418, 440 nm EL: 416 nm, <u>Blue violet</u>	UV: 366 nm, PL: 424 nm <u>Blue violet</u>	
			
a , R = H; UV: 438 nm, PL: 485, 512 nm EL: 480 nm, <u>Greenish blue</u> b , R = CH ₃ ; UV: 384 nm, PL: 460 nm EL: 468 nm, <u>Pale blue</u>	UV: 427 nm, PL: 548 nm EL: 545 nm, <u>Green</u>	UV: 446 nm, PL: 510 nm <u>Greenish blue</u>	
			
UV: 444 nm, PL: 494, 526 nm EL: 588 nm, <u>Pale yellow</u>	UV: 517 nm, PL: 532, 574 nm EL: 536 nm, <u>Green</u>		

	Comp. 293
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TPD

Huang's group has systematically studied the structure-property relationships of fluorene-thiophene based conjugated polymers **Comp. 294–Comp. 297**.^{373,374,375} In contrast to polythiophene homopolymers (see next section), the regioregularity of the bithiophene fragments in the studied copolymers show little influence on the optical band-gap (**Comp. 296** and **Comp. 297**, respectively: $E_g = 2.49$ and 2.58 eV³⁷⁴, or 2.57 and 2.60 eV^{376,377}) or the emission maxima, but the head-to-head copolymer **Comp. 297** was significantly more thermally stable.

 <p>UV: 412 nm, PL: 492, 477 nm <u>Bluish green</u></p>	 <p>UV: 378 nm, PL: 458, 475 nm <u>Blue</u></p>	Comp. 294 Comp. 295 Comp. 296 Comp. 297
 <p>UV: 403 nm, PL: 490, 520 nm <u>Green</u></p>	 <p>UV: 401 nm, PL: 493, 520 nm <u>Green</u></p>	

All co-polymers showed reversible both *n*- and *p*-doping in CV experiments, and a schematic diagram showing the HOMO and LUMO energy levels relative to the work function of the electrode materials used in EL devices are given in Figure 21.³⁷⁷ The single layer ITO/**Comp. 297** (100nm)/Ca device emitted green light (493, 515 nm) with high turn-on voltage of 20 V. The introduction of PVK hole transport layer decreased turn-on voltage to 8 V and increased the maximum external Q.E. from 0.05 % to 0.6 %^{373,375} (although less pronounced increase was observed for other polymers of the series³⁷⁷). Later this group reported somewhat lower EL Q.E. of 0.3 % for the device ITO/PVK/**Comp. 297**(75 nm)/Ca/Al. The highest EL Q.E. in this series was reported for **Comp. 294** (0.64 % for ITO/PVK/**Comp. 294**/Ca/Al) and the lowest one was for **Comp. 296** (0.07 % for ITO/PEDOT/**Comp. 296**/Ca/Al).³⁷⁷ Noteworthy, this trend has no correlation with the polymer energy levels.

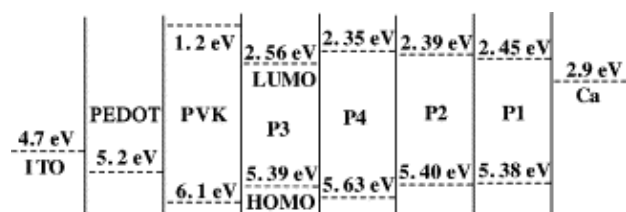


Figure 21. The schematic energy level structure for the devices with co-polymers **Comp. 294–Comp. 297** (on the diagram, polymers P3, P4, P1 and P2, respectively) [ref. 377, © 2002 Elsevier].

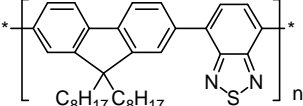
An increase in the PL quantum efficiency of the fluorene-thiophene co-polymers can be achieved by introduction of *S*-oxidized thiophene units (although no efficient EL from such materials have been reported). This aspect and the chemical structures of *S,S*-thiophenedioxide/fluorene co-polymers are discussed in more detail in "Polythiophenes" section.

A very efficient green-emitting fluorene co-polymer **Comp. 298** was synthesized by Lim et al. via Suzuki coupling of dibromothieno[3,2-*b*]thiophene with dialkylfluorenediboronic acid.³⁷⁸ The authors compared the EL properties of this co-polymer with PFO homopolymer **Comp. 188** and PFO-bithiophene co-polymer **Comp. 289**. Both the absorption and emission spectra of **Comp. 298** are red-shifted compared with PFO **Comp. 188** but slightly blue-shifted compared to bithiophene-based co-polymer **Comp. 289**. PLED fabricated in configuration ITO/PEDOT/**Comp. 298**/LiF/Al showed a pure green emission (CIE: *x* = 0.29, *y* = 0.63) close to the standard NTSC green color (CIE: *x* = 0.26, *y* = 0.65) with a very low turn on voltage of 3.3 V. The low turn on voltage is attributed to the better

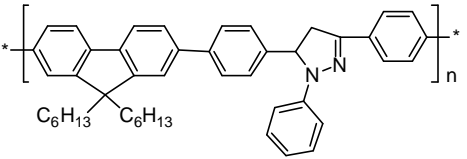
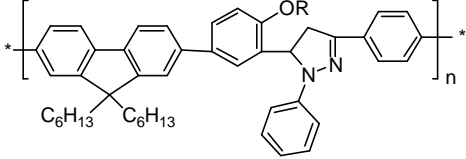
(comparing to PFO) match between the HOMO (−5.38 eV) level with the workfunction of PEDOT (5.1–5.3 eV). Interestingly, although the PL quantum yield of **Comp. 298** (12% in films, similar to **Comp. 289**) is lower than that of PFO (55%), the EL efficiency is much higher, which may reflect an improved balance of electron/hole transport in this co-polymer. The maximum current efficiency of **Comp. 298** is 0.32 cd/A at 0.78 A/cm², which exceeds the performance of similar devices fabricated with **Comp. 289** or PFO **Comp. 187** (which showed 0.20 cd/A at 143 mA/cm² and 0.06 cd/A at 25 mA/cm², respectively). The external Q.E. of **Comp. 298** (0.1%) was twice as high as for the former polymers.

 <p>UV: 448, 471 nm, PL: 495, 511, 548 nm EL: 515 nm, <u>Green</u> CIE (0.29, 0.63)</p>	Comp. 298
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A green-emitting fluorene-benzothiadiazole co-polymer **Comp. 299** was synthesized at Dow Chemical by Suzuki coupling of fluorene-2,7-diboronic acid with dibromobenzothiadiazole.^{379,216} A high performance green emission PLED was demonstrated with this co-polymer.³⁸⁰ Since this co-polymer has the electron-deficient moiety in the polymer backbone, a stable anode electrode such as Al can be used, although a thin (70 Å) HTL (TPD, **Comp. 293**) should be introduced for optimal EL performance. Double layer PLED device fabricated in configuration ITO/**Comp. 293**/**Comp. 299**/Al showed green emission with a turn on voltage of 7.0 V. The maximum external Q.E. as high as 3.86 % (peak efficiency 14.5 cd/A) and brightness of 5,000 cd/m² was achieved at current 34 mA/cm². Even higher performance (external Q.E. 5%, efficiency >20 lm/W, brightness 10,000 cd/A) for this polymer was reported by Millard at CDT company, although the exact LED structure was not disclosed.³⁸¹ Besides, the EL device with **Comp. 299** exhibited excellent electrical stability even when operated at high current densities (> 0.25 A/cm²). When blended with PFO **Comp. 188**, an efficient Förster energy transfer from excited PFO segments to **Comp. 299** chain is observed.³⁸²

 <p>UV: 390 nm, PL: 540 nm, EL: 545 nm, <u>Green</u> CIE (0.394, 0.570)</p>	Comp. 299
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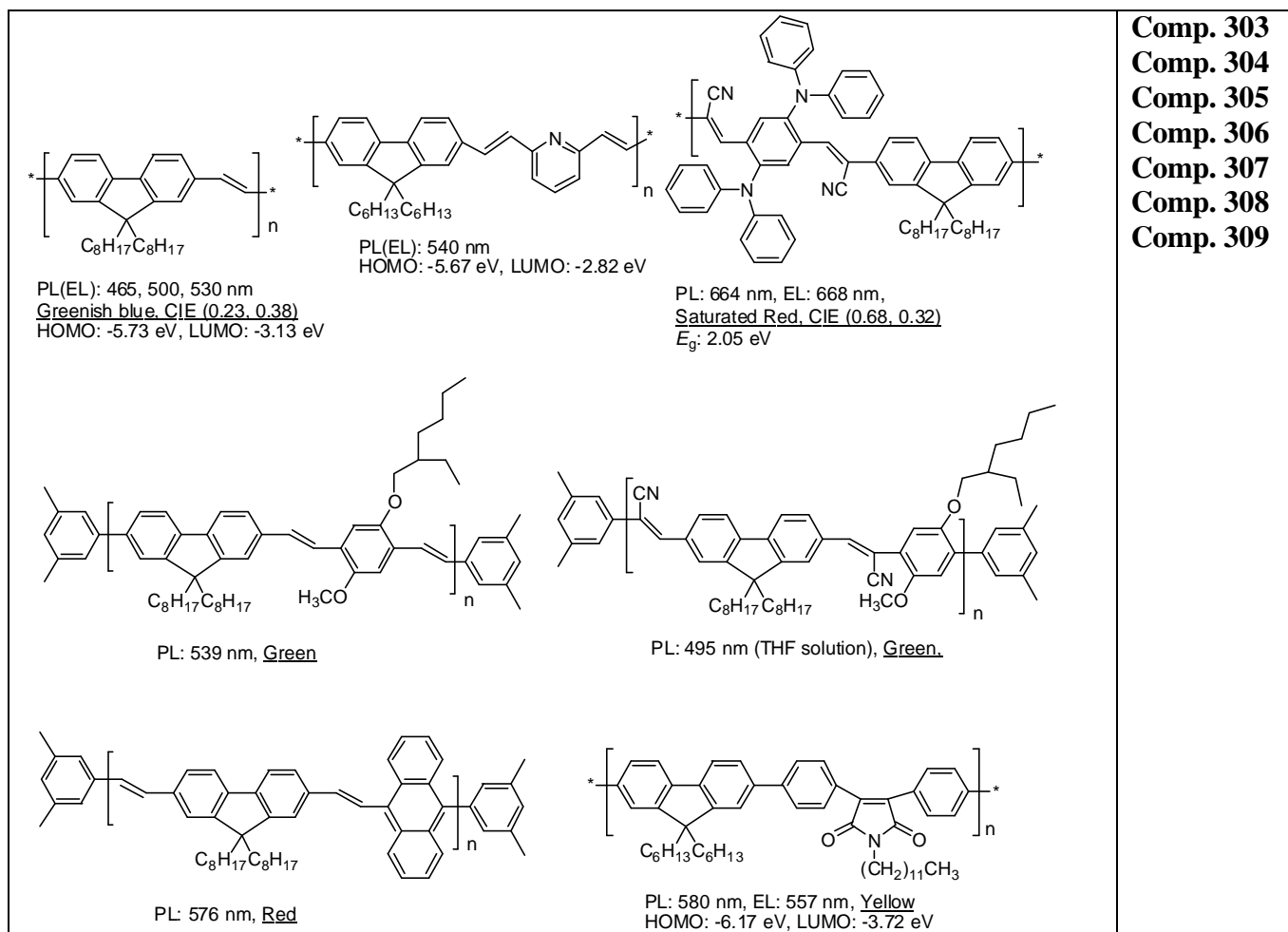
Green emitting fluorene co-polymers **Comp. 300** and **Comp. 301** were also obtained by introducing pyrazoline moiety into a backbone, which completely interrupt the conjugation due to sp³ hybrid carbons in the ring.³⁸³ Polymers emit green light with PL efficiency of 49–59 % in films. The PLEDs ITO/PEDOT/polymer/Ba/Ca showed bright green emission at λ_{EL} = 494–500 nm with external quantum efficiencies of 0.6–2.5 %, low turn-on voltage (3.7–5.5 V) and brightness of up to 2,400 cd/m².

 <p>UV: 339, 395 nm, PL: 508, <u>Green</u></p>	 <p>a, R = C₆H₁₃; UV: 337, 399 nm, PL: 508, <u>Green</u> b, R = C₁₂H₂₅; UV: 336, 398 nm, PL: 508, <u>Green</u></p>	Comp. 300 Comp. 301a,b
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Introduction of electron-accepting bithieno[3,2-*b*:2',3'-*e*]pyridine units resulted in co-polymer **Comp. 302** with ca. 0.5 V lower reduction potential, as compared to parent homopolymer PFO **Comp. 187**.³⁸⁴ Upon excitation at 420 nm ($\lambda_{\text{abs}}^{\text{max}} = 415$ nm) co-polymer **Comp. 302** exhibited blue-green emission with two peaks at 481 nm and 536 nm. Preliminary EL studies of ITO/PEDOT/**Comp. 302**/Al device showed two peaks positioned as in PL spectra. The PLED exhibited low turn-on voltage (~ 4 V) and at higher voltages of 6–9 V a slight relative increase of the green component was observed.



Various fluorene–phenylenevinylene alternating co-polymers with different emission color have been synthesized, e.g.: **Comp. 303**,^{385,386} **Comp. 304**,³⁸⁷ **Comp. 305**,¹⁵⁰ **Comp. 306**, **Comp. 307**, **Comp. 308**,³⁸⁸ and **Comp. 309**³⁸⁹ (Scheme 46).



Scheme 46. Fluorene/phenylenevinylene co-polymers and their optical/electronic properties in the solid state.

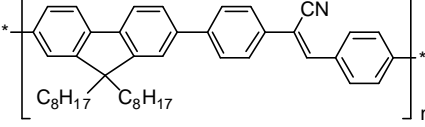
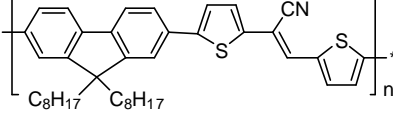
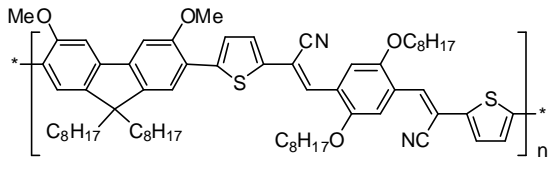
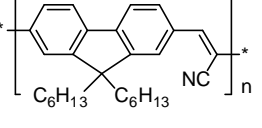
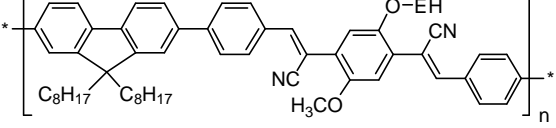
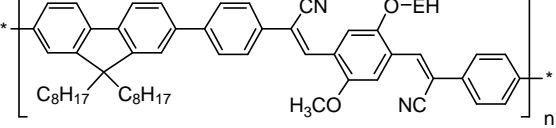
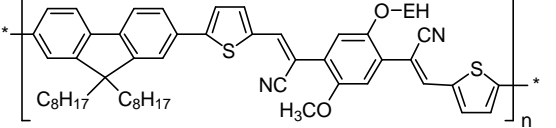
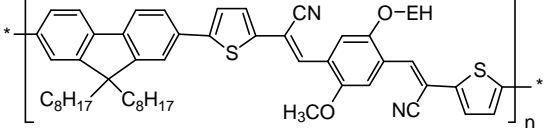
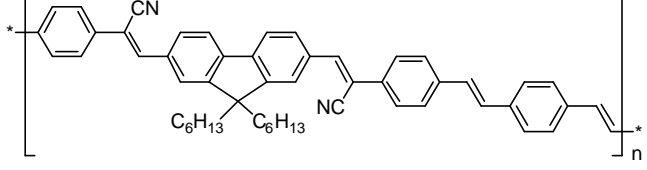
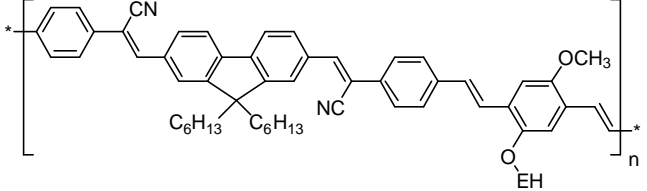
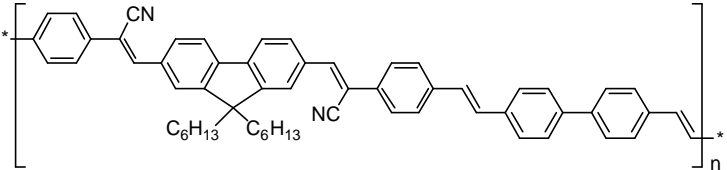
Introducing electron-rich (as in polymers **Comp. 306** and **Comp. 308**), electron deficient (as in compounds **Comp. 304**, **Comp. 309**, and **Comp. 321–Comp. 323**), or both of these units (as in compounds **Comp. 305** and **Comp. 307**) in the PF chain allows for precise tuning the emission wavelength (Scheme 46), the HOMO/LUMO levels and the charge injection/transport properties. However, no high-performance PLED based on the above co-polymers have yet been reported. One of the best performing devices built in configuration ITO/PEDOT/**Comp. 303**/Ca/Al showed the maximal brightness of 870 cd/m² (at 10 V) and the EL efficiency of only 0.16 cd/A.

Several fluorene-containing arylene-vinylene co-polymers with a cyano-group attached to the vinylene fragment have been reported. The co-polymer **Comp. 310**, containing cyanovinylene-phenylene segments in the main chain, in contrast to red-emitting co-polymers CN-PPV,¹⁵³ emitted blue light with narrow bandwidth (FWHM = 71 nm).³⁹⁰ The ITO/PVK:**Comp. 310**/Alq₃/Al device reached brightness 784 cd/m² at a bias voltage of 18 V and an external Q.E. of 0.2 % (at 123 mA/cm²).

Its structural analog **Comp. 311** in which the benzene ring is replaced with thiophene showed substantial red shifts in both absorption (97 nm) and emission (134 nm) spectra, and PLED based on this co-polymer (ITO/LiF/**Comp. 311**/PBD/LiF/Al/Ag) emitted red-orange light (brightness of 45 cd/m² at 10 V; turn-on voltage of 5 V).³⁹¹ Further bathochromic shift in the PL (pure red emission) was observed in co-polymer **Comp. 312**, for which HOMO (−5.32 eV) and LUMO (−3.32 eV) energies were calculated from electrochemical data (both oxidation and reduction appeared as quasi-reversible processes).²⁹⁹ No devices have been fabricated with this co-polymer. Green-emitting polymer **Comp. 313** ITO/PEDOT/**Comp. 313**/Al device showed turn-on voltage of 4.8 V, a brightness of 600 cd/m² (at 5.8 V) and maximal power efficiency of 0.85 lm/W (at 5.6 V).³⁹²

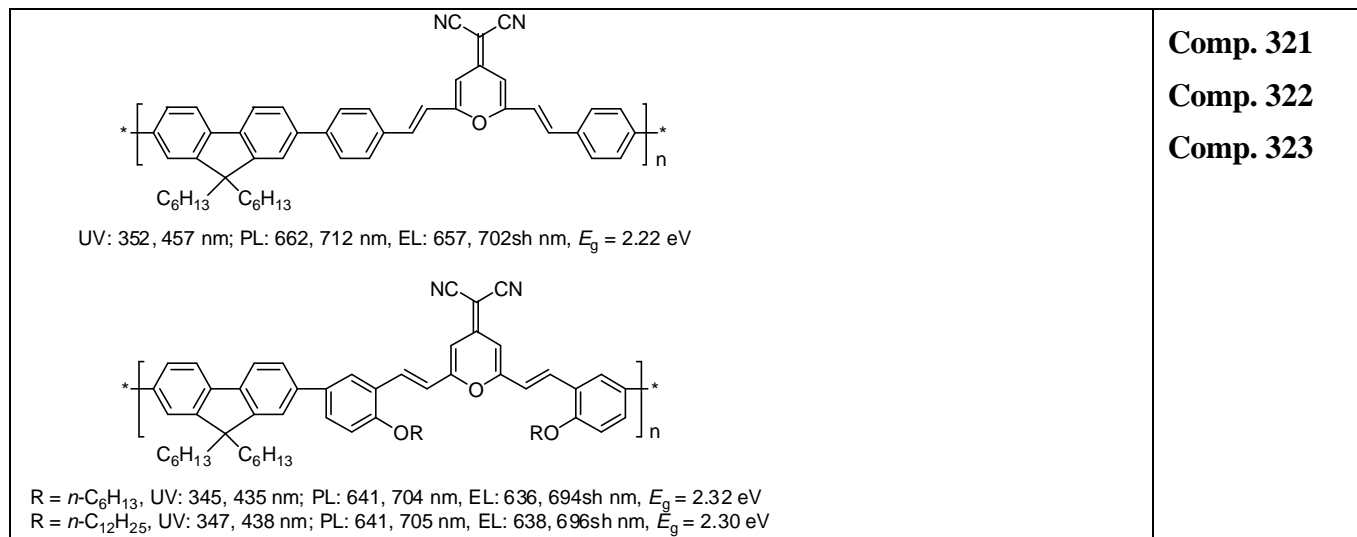
A series of four fluorene-phenylenevinylene copolymers **Comp. 314–Comp. 317** clearly demonstrate the effect of the exact position of CN groups in the vinylene fragment on the emission of the materials (Scheme 47).³⁹³ Substitution of benzene rings in copolymers **Comp. 314** and **Comp. 315** by thiophene ring results in red shift of PL and EL and copolymers **Comp. 316** and **Comp. 317** exhibit pure red emission with chromaticity values very close to the standart red (CIE, $x = 0.66$, $y = 0.34$), although no PLQY values have been reported. The ITO/PEDOT/**Comp. 316**/Ca/Al device showed ver low turn-on voltage of 2.6 V and maximum brightness of 3,100 cd/m² at 6 V. Its maximum external Q.E. was 0.46 % at 4 V, with a brightness of 652 cd/m².

Yellow to orange emission was observed in another series of fluorene-phenylene copolymers with CN groups at vinylene fragment **Comp. 318–Comp. 320** (Scheme 47).³⁹⁴ The PLQY of the copolymers was relatively low (from 3.5 % for **Comp. 320** to 14.7 % for **Comp. 319**) and the best results in PLED testing were achieved for copolymer **Comp. 319**. The device ITO/PEDOT/**Comp. 319**/Al showed turn-on voltage of 5.0 V and maximum brightness of 7.500 cd/m² at 20 V, with maximum luminance efficiency of 0.21 lm/W at 6.7 V.

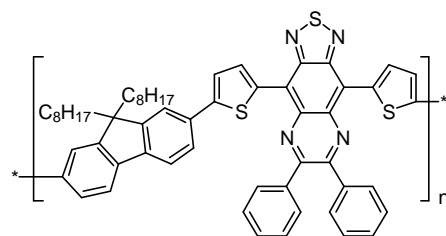
 <p>UV: 403 nm, PL: 476 nm, EL: 466 nm (FWHM 71 nm) <u>Blue</u></p>	 <p>UV: 500 nm, PL: 610 nm, EL: 610 nm <u>Red-orange</u></p>	<p>Comp. 310 Comp. 311 Comp. 312 Comp. 313</p>
 <p>UV: 563 (601) nm, PL: 656 (702) nm <u>Red</u></p>	 <p>UV: 440 nm, PL: 535 nm EL: 535 nm <u>Green</u></p>	
 <p>UV: 372 nm, PL: 525 nm, EL: 547 nm, <u>Yellowish-green</u>, CIE (0.40, 0.53)</p>	 <p>UV: 468 nm, PL: 555 nm, EL: 554 nm, <u>Yellow-orange</u>, CIE (0.48, 0.51)</p>	<p>Comp. 314 Comp. 315 Comp. 316 Comp. 317</p>
 <p>UV: 460 nm, PL: 602 nm, EL: 604 nm, <u>Red</u>, CIE (0.63, 0.38)</p>	 <p>UV: 537 nm, PL: 674 nm, EL: 674 nm, <u>Red</u>, CIE (0.66, 0.33)</p>	
 <p>UV: 419 nm, PL: 591 nm, EL: 599 nm, <u>Yellow-orange</u>, CIE (0.48, 0.48)</p>		<p>Comp. 318 Comp. 319 Comp. 320</p>
 <p>UV: 439 nm, PL: 602 nm, EL: 596 nm, <u>Orange</u>, CIE (0.53, 0.44)</p>		
 <p>UV: 417 nm, PL: 551, 580sh nm, EL: 557, 585 nm, <u>Yellow</u>, CIE (0.43, 0.45)</p>		

Scheme 47. Fluorene/phenylene-vinylene co-polymers with CN groups at vinylene fragment, and their optical and electronic properties in the solid state.

Another series of red-emitting fluorene-containing co-polymers of arylene-vinylene type was obtained by introducing 4-dicyanomethylenepyrene-2,6-diyl moiety in the main polymeric chain (**Comp. 321–Comp. 323**).³⁹⁵ The PL and EL spectra revealed a broad band at 600–800 nm and no emission from the fluorene segments (expected at ~450 nm). The PLEDs fabricated as ITO/PEDOT/Polymer/Ba/Al emitted red light with maximum external Q.E. of 0.21–0.38 %, quite high turn-on voltages (10.4–11.7 V), and brightness of ~200–450 cd/m² at a bias voltage of ~16–18 V.

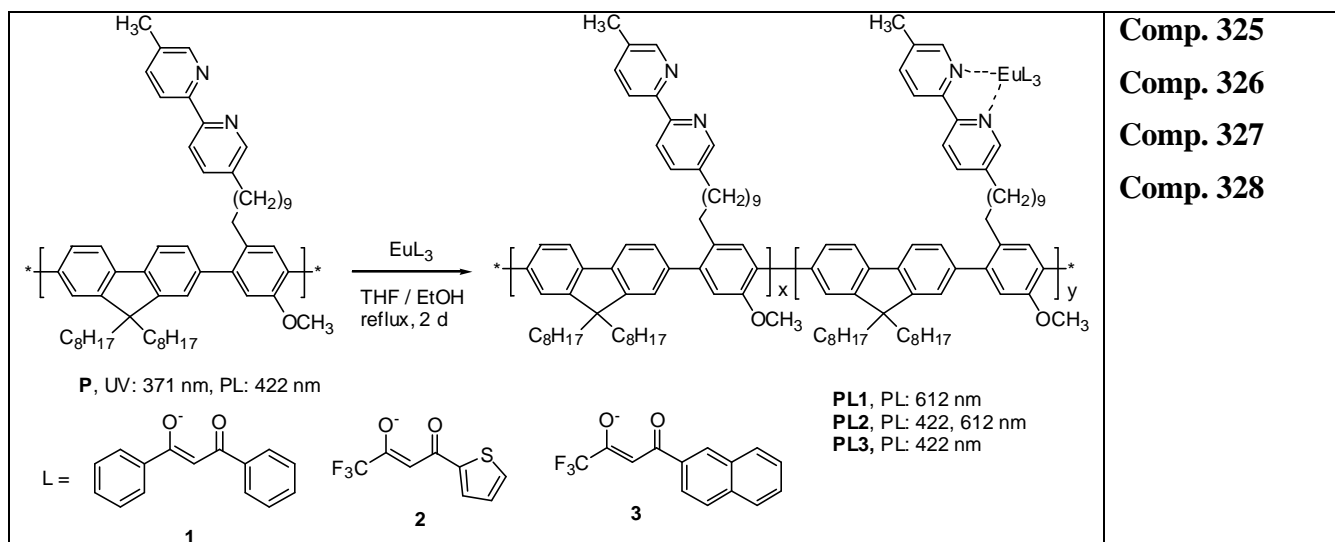


PL and EL emissions from a very low-bandgap co-polymer **Comp. 324** ($E_g = 1.27$ eV) was demonstrated by Swedish researchers.³⁹⁶ The material has two absorption peaks at 400 and 780 nm and emits the light in the NIR region. The PL spectrum of thin films has one peak at 1035 nm, which is blue-shifted by ca. 60 nm on annealing at 200 °C for 10 min. The ITO/PEDOT/**Comp. 324**/Ca/Al diode was positively biased when the Al/Ca electrode was connected to lower potential and the EL emission become observable at as low as 1.1 V ($\lambda_{EL} = 970$ nm). The external Q.E. for non-optimized device was quite low (0.03–0.05 %), nevertheless demonstration of EL from PLED in NIR region can be important for communication and sensor technologies.

**Comp. 324**

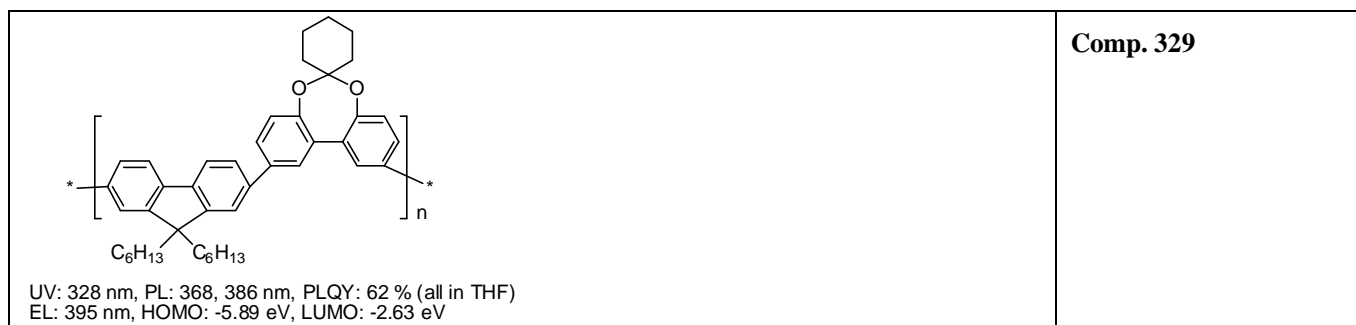
UV: 400, 780 nm, PL: 1035 nm, EL: 970 nm, NIR

Pei et al. reported an alternating fluorene co-polymer **Comp. 325** with 2,2'-bipyridyl in a side chain, which emits at 422 nm. Treating this polymer with Eu³⁺ chelates forms the polymeric complexes **Comp. 326–Comp. 328**. Their emission is governed by intramolecular Förster energy transfer, which efficiency depends on the structure of the ligands and the content of Eu³⁺ (Scheme 48.).³⁹⁷ The most effective energy transfer manifested in a single red emission band at 612 nm was observed for the complex **Comp. 326** with a maximum intensity achieved at ~25 mol.% content of Eu³⁺.



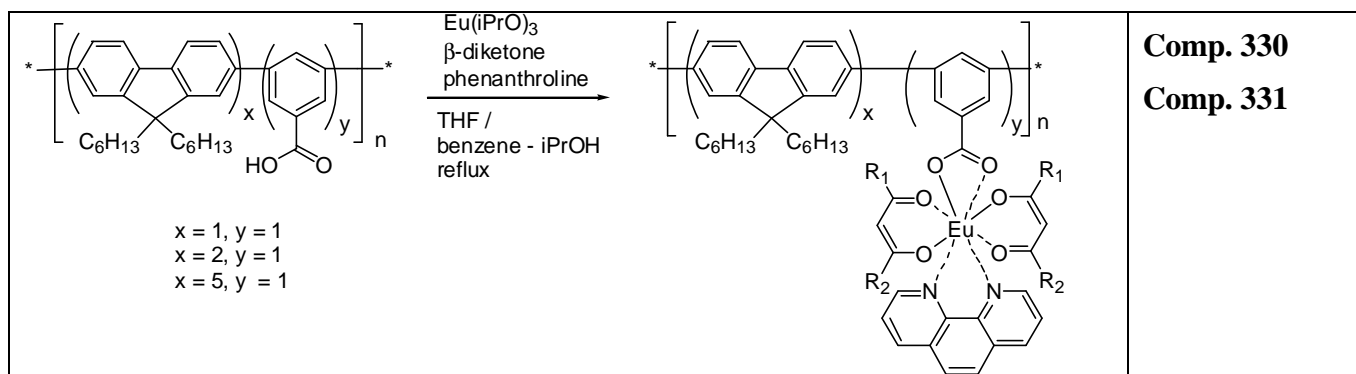
Scheme 48. Synthesis of Eu-contained chelated PFs.

The color of fluorene copolymers can be also shifted into UV region, as exemplified by copolymer **Comp. 348**.³⁹⁸ Its PL spectrum in THF solution is blue-shifted for 49 nm as compared to PDHF **Comp. 187** showing somewhat lower PLQY (62%). The ITO/PEDOT/**Comp. 348**/Ba/Al device emits violet light with $\lambda_{\text{EL}}^{\text{max}} = 395$ nm) with, however, bad performance (turn-on voltage 8 V, maximum external Q.E. 0.054 %, brightness 10 cd/m²). When it was blended with 5% PDHF **Comp. 187**, the maximum external Q.E. increased to 0.3 % (slightly lower than for pure PDHF **Comp. 187** measured in the same conditions) and the color purity was improved (CIE $x = 0.18$, $y = 0.10$). *[I did not get, which color purity??]*



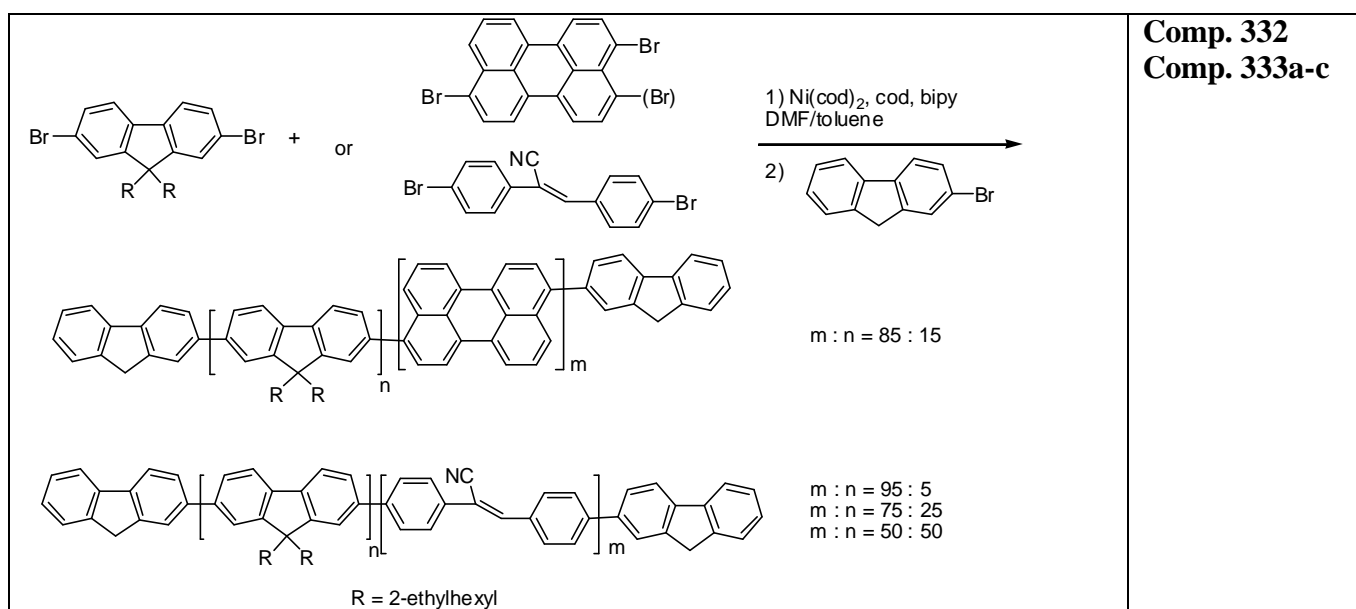
2.11.3 Random (Statistical) Co-polymers.

Another example of efficient Förster energy transfer in Eu³⁺ complexes of fluorene co-polymers (similar to described alternating co-polymers in Scheme 48) was demonstrated by Huang et al. for random co-polymers. They synthesized co-polymers **Comp. 330** with different ratio between the fluorene and the benzene units in the backbone, and converted them into europium complexes **Comp. 331** (Scheme 49).³⁹⁹ The complexes **Comp. 331** were capable of both blue and red emission under UV excitation. In solution blue emission was the dominant mode, however, the blue emission was significantly reduced or completely suppressed in the solid state and nearly monochromatic (FWHM \approx 4 nm) red emission at 613 nm was observed.



Scheme 49. Synthesis of polymeric Eu complex **Comp. 331**. β -Diketonate ligands are the same as in complexes **Comp. 326–Comp. 328** (Scheme 48).

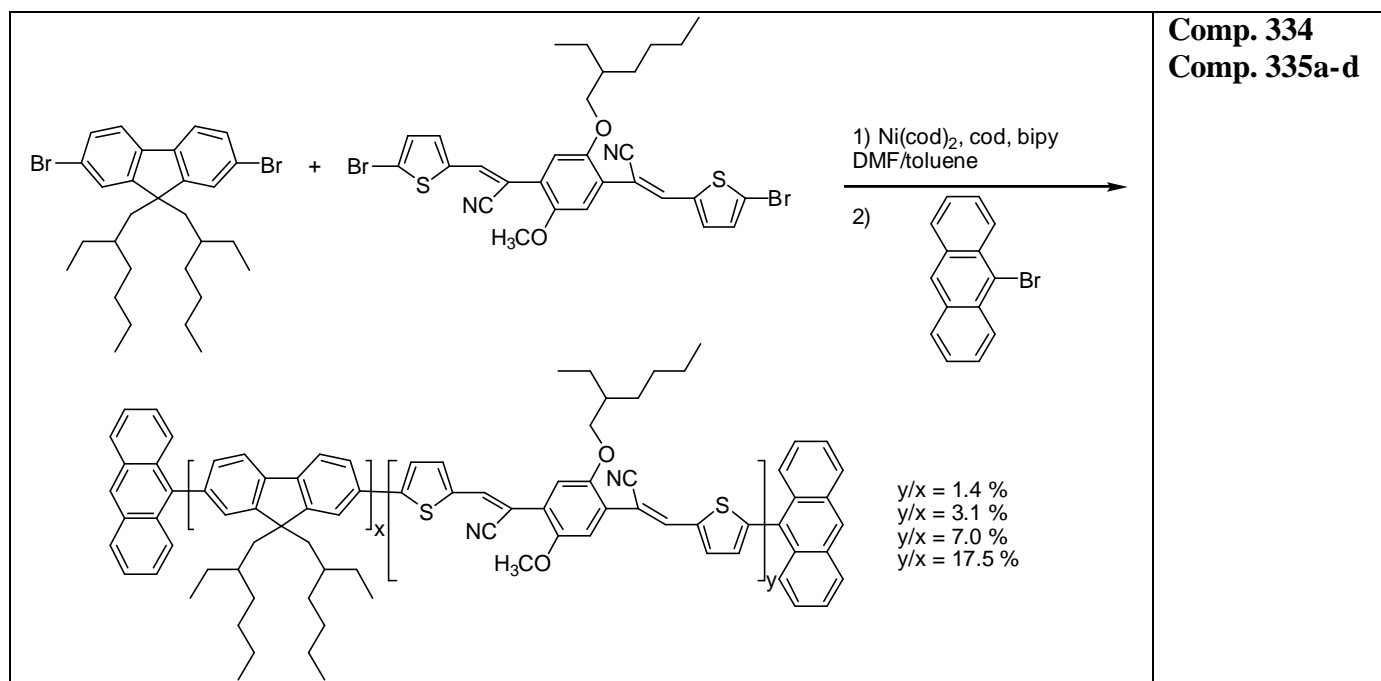
Miller's group at IBM reported two series of statistical PF co-polymers using perylene and cyano-substituted phenylenevinylene chromophoric segments (Scheme 50).^{400,401,402}



Scheme 50. Synthesis of perylene–fluorene and α -cyanostilbene–fluorene co-polymers via Yamamoto coupling.

The co-polymers **Comp. 332** and **Comp. 333** are soluble in organic solvents and their molecular weights are in the range of $M_n \sim 10,000\text{--}55,000$ g/mol. They are thermally stable and show no color change after the thermal annealing. The emission color is strongly dependent on the feed ratio of the co-monomers. For example, in the case of co-polymers **Comp. 333**, the emission color can be tuned from blue (**Comp. 333a**, 466 nm) through blue- green (**Comp. 333b**, 481 nm), to pure green (**Comp. 333c**, 510 nm).

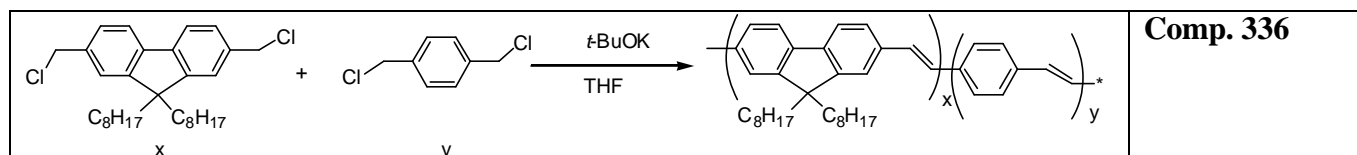
Following that, Shim et al. reported a series of random co-polymers synthesized by Yamamoto coupling of 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene with **Comp. 334** (Scheme 51).^{403,404}



Scheme 51. Synthesis of PF-PPV co-polymer **Comp. 335** with tunable emission color.

Varying the feed ratio of the thiophene co-monomer from 1:99 to 15:85, green, yellow and red emitting co-polymers have been synthesized. The actual ratio of the co-monomer, calculated from the analysis of nitrogen, is somewhat higher than the feed ratio, reflecting a higher reactivity of **Comp. 334** monomer in the Yamamoto reaction. All the co-polymers are soluble in common organic solvents, and the molecular weight (M_n) is in the range of 13,000–22,000 g/mol (PDI = 1.5–2.7). Interestingly, regardless of the composition, all the co-polymers showed a similar absorption with λ_{max} at ~380 nm, with exception of a weak shoulder at ~470 nm, which is more intense for polymers with higher ratio of **Comp. 334** unit. In contrast, their emission colors are progressively red-shifted with increasing the fraction of co-monomer **Comp. 334**. As a result, **Comp. 335a** emits green (540 nm), **Comp. 335b** emits yellow (585 nm), and **Comp. 335c** emits bright red (620 nm), all with reasonably high photoluminescent quantum yield (34–69%). The electroluminescence spectra obtained from PLEDs fabricated as ITO/PEDOT/Polymer/LiF/Al are almost identical to the PL spectra. As the feed ratio of **Comp. 334** increases, the threshold voltage drops from 13 to only 5 V, and the emission intensity at low voltages also increases, which suggests improved charge-transport balance in the material. As can be calculated from the current–voltage–luminance (I – V – L) plot, the luminous efficiency of ~0.7 cd/A (at 15 V), ~2.4 cd/A (at 12 V) and ~1.5 cd/A (at 9.5 V) is achieved with polymers **Comp. 335a,b,c**, respectively.

Hwang et al. reported random co-polymers of polyfluorene with PPV units in different feeding ratio through Gilch polymerization (Scheme 52).³⁸⁶



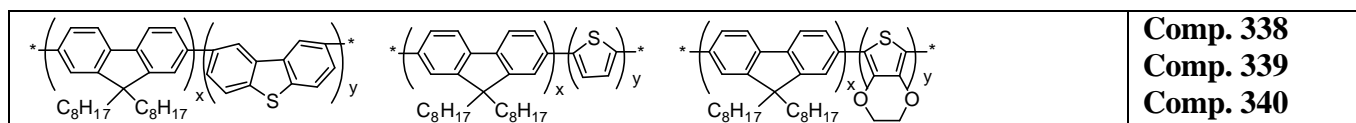
Scheme 52. Gilch polymerization to synthesis of random co-polymers.

The molecular weights of the obtained co-polymers are in the range of 57,000–87,000 g/mol with PDI of 1.4 to 2.1. Interestingly, the co-polymers **Comp. 336** with different feed ratio $x:y$ showed the same optical properties as those of the corresponded fluorene-vinylene homopolymer ($y = 0$, **Comp. 303**). The UV-vis spectrum of the thin films showed the peak absorption at 418 nm with onset absorption of 485 nm and the PL emission had a maximum at 470 nm plus well-defined vibronic bands at 500 nm, 530 nm and 560 nm. PLED devices fabricated by ITO/PEDOT/**Comp. 336**/Al gave very similar EL emission spectrum (CIE: $x = 0.23$; $y = 0.38$) and significantly improved device performance (0.71–1.05 cd/A) as compared to the homopolymer **Comp. 303** (0.13 cd/A). The latter is explained by improved hole injection and transport, owed to introduced PPV segments. Indeed, the ionization potential of the co-polymers is around 5.53–5.55 eV, which is much closer to the HOMO level of PEDOT (5.2 eV), as compared to homopolymer (5.73 eV).

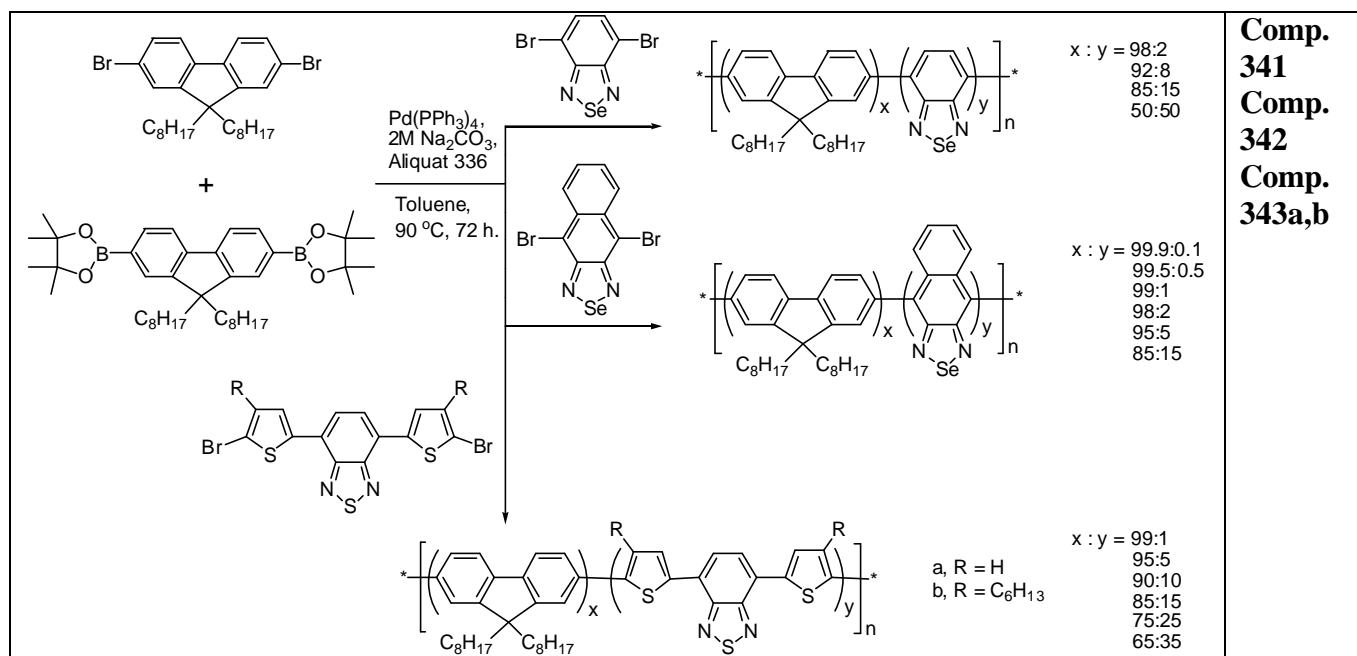
The emission wavelength of PF-PPV co-polymer can be red-shifted and the band gap shrank by introducing alkoxy substituents, as demonstrated for compound **Comp. 337**.⁴⁰⁵ Consequently, the transport of both holes and electrons is facilitated and the PLED built in configuration ITO/PEDOT/**Comp. 337**/Al produces an orange-red color ($\lambda_{EL} = 580$ nm) with maximum brightness of 1,350 cd/m² and luminous efficiency of 0.51 cd/A, at rather low turn-on voltage 2.5 V.



Several random fluorene-thiophene co-polymers such as **Comp. 338**,^{406,407} **Comp. 339**,⁴⁰⁸ **Comp. 340**,^{408,409} have been investigated. Because of possibility of fine tuning the co-monomers ratio, many of these have shown the EL performance far greater than that of PF homopolymer or the corresponding alternating co-polymers. Thus, the PLED ITO/PEDOT/**Comp. 339**/Ba/Al shows the brightness of ca. 2,600 cd/m² (at 8 V) and the external Q.E. of 1.25%. The “meta” linkage in the dibenzothiophene in co-polymer **Comp. 338** limits the effective conjugation length, and bounds the emission bands in deep-blue color range ($\lambda_{max} \sim 420$ and 440 nm).⁴⁰⁶ Furthermore, hindered conjugation (within the chain) and π -aggregation (between the chain) suppress the parasitic green emission at 520 nm in the solid state of the polymer.



Cao and co-workers synthesized several co-polymers **Comp. 341**, **Comp. 342**, and **Comp. 343a,b** exploiting random co-polymerization of fluorene fragments with dibromo derivatives of Se,N and S,N heterocycles (Scheme 53).^{410,411,412,413}



Scheme 53. Synthesis of benzothiaselenazole-, naphthoselenathiazole- and (thiophene-benzothiazole-thiophene)-fluorene co-polymers via Suzuki coupling.

Fluorene-benzoselenadiazole alternating co-polymer **Comp. 341** (x:y = 50:50) showed substantial (55 nm) red shift in PL, as compared to its benzothiadiazole analog **Comp. 299** (595 nm⁴¹⁰ and 540 nm,^{380,296} respectively) because of a narrower π - π^* gap of the benzoselenadiazole unit. Increasing the content of the fluorene moieties in the co-polymers **Comp. 341** results in a regular blue shift of PL (568 nm for x:y = 98:2), though an irregular variations in Φ_{PL} (between 16 and 51 % in films) were reported for this series of co-polymers. Whereas the main PL in solution is observed in the region of 570–600 nm with a low intensity short-wavelength band (due to fluorene emission), the latter is completely suppressed in films. PLEDs fabricated as ITO/PEDOT (or PVK)/**Comp. 341**/Ba/Al showed orange-red emission (λ_{EL}^{max} = 573–600 nm, depending on the x:y ratio) with no blue emission even at the lowest concentration (2%) of the heterocyclic inits. Comparison of devices with two different HTL (PEDOT or PVK) showed that LED with PVK layer (ITO/PVK/**Comp. 341** (x:y = 85:15)/Ba/Al) demonstrates a better external Q.E., which reached the value of 1 % (λ_{EL}^{max} = 582 nm; CIE: x = 0.698, y = 0.300).⁴¹⁰

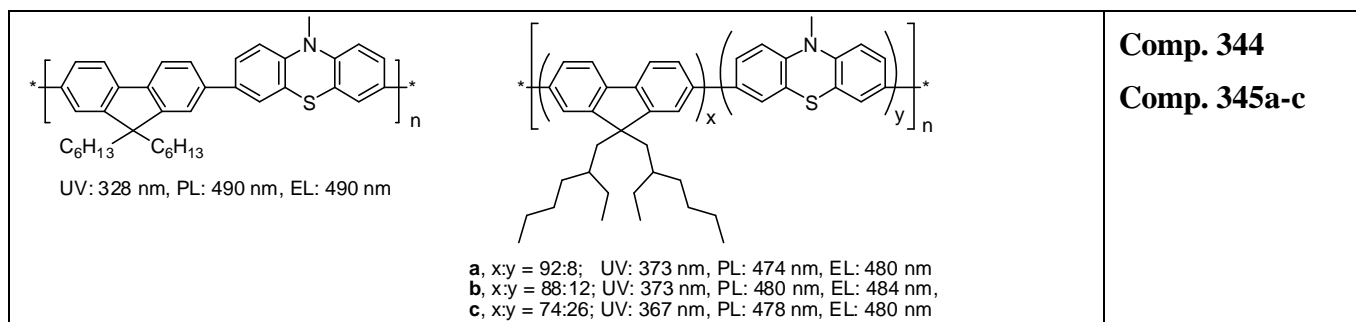
Further pronounced bathochromic shift in emission was achieved for co-polymers **Comp. 342**, which emit in the red region with λ_{PL} = 634–681 nm (Φ_{PL} = 33–84 %). Although the blue emission at 423–438 nm from the fluorene fragments is also observed, its intensity decreased with decrease of the x:y ratio.⁴¹¹ In EL spectra the blue emission from the PF segment was completely quenched at very low naphthoselenadiazole content (0.5 %), which could be due to efficient exciton/charge trapping on narrow-band-gap naphthoselenadiazole sites. The highest external Q.E. of 3.1 % was reported for ITO/PEDOT/**Comp. 342** (x:y = 99:1)/Ba/Al diodes (although it corresponds to a relatively low luminous efficiency of 0.91 cd/A due to unfavorable for a human eye spectra distribution) and the maximal brightness was up to 2,100 cd/m² (CIE: x = 0.64, y = 0.33).

The last example of red-emitting fluorene co-polymer in this series, the co-polymers **Comp. 343a,b** contains both benzothiadiazole acceptor and thiophene donor units in the main chain.^{412,413} As expected for an alternating donor-acceptor conjugated polymer, a substantial red shift in PL as compared to co-polymer **Comp. 299** or even **Comp. 341** was observed [λ_{PL} = 635–685 nm (**Comp.**

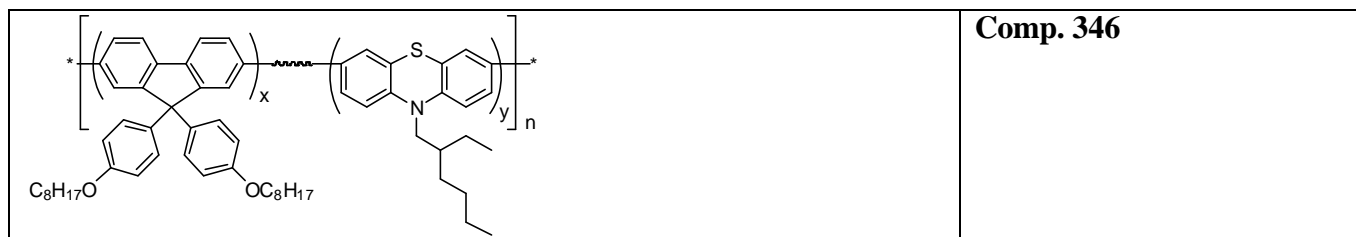
343a),⁴¹² 629–678 nm (**Comp. 343b**)⁴¹³ in films, for x:y 99:1 –65:35). Again, observed in diluted solution additional emission from fluorene segments is completely suppressed by increasing the polymer concentration or the content of heterocyclic fragment in the polymer chain.

ITO/PEDOT/**Comp. 343**/Ba/Al devices showed external Q.E. in the range of 0.5–1.4 %. The highest efficiency of 1.4 % and the luminance of 256 cd/m² at a bias of 5.1 V was achieved for the co-polymer having x:y = 85:15 ratio. This device reached maximum luminance of 3,780 cd/m² at 8.2 V. Even higher external Q.E. of 1.93–2.54 % was achieved with copolymers **Comp. 343b** (x:y = 95:5 to 85:15) for the device ITO/PEDOT/PVK/**Comp. 343b**/Ba/Al.⁴¹³ These copolymers showed saturated red emission with $\lambda_{EL} = 634\text{--}647$ ($x = 0.66\text{--}0.67$, $y = 0.33\text{--}0.34$).

Jenekhe et al. synthesized a phenothiazine-containing alternating fluorene co-polymer **Comp. 344** by Suzuki-coupling polymerization.⁴¹⁴ The phenothiazine-3,7-diyl fragment in the polymer backbone interrupts the conjugation which is manifested by substantial blue shift in absorption as compared to PDHF homopolymer **Comp. 187** (328 and 385 nm, respectively). Nevertheless, the ionization potential of the **Comp. 344** (estimated from the electrochemical data as $I_p = E_{ox}^{onset} + 4.4$ V) is much higher (5.1 eV) than that for **PDHF Comp. 187** due to electron-rich phenothiazine unit, suggesting good hole transport properties. Greenish-blue EL ($\lambda_{EL}^{max} = 490$ nm) with luminance of up to 320 cd/m² and a maximum external Q.E. of 0.10 % at 12.5 V was observed for the ITO/PEDOT/**Comp. 344**/Al diode. Similar random fluorene/phenothiazine co-polymers **Comp. 345a-c** showed close EL maxima, but much better device performance (e.g. for **Comp. 345b**: maximum brightness 4,170 cd/m², power efficiency 2.08 cd/A, turn-on voltage 3.8 V; CIE: $x = 0.17$, $y = 0.37$).⁴¹⁵



Hwang et al. studied EL from the devices fabricated using blends of similar blue-emissive fluorene-phenothiazine co-polymer **Comp. 346** with MEH-PPV.⁴¹⁶ The maximum brightness of the devices ranged from 1,580 to 2,640 cd/m² with external Q.E. of 0.3 to 0.4%. The inefficient energy transfer between these blue and red LEP enabled the production of white light emission through control of the blend ratio: with increase of the amount of **Comp. 346** in the blends CIE coordinates of EL emission are shifted from $x = 0.19$, $y = 0.45$ (for 1% of **Comp. 346**) to $x = 0.36$, $y = 0.51$ (for 3% of **Comp. 346**), although even the most optimal blend (2.5% of **Comp. 346**: $x = 0.19$, $y = 0.45$) is quite far from the real white point.



Müllen et al. achieved efficient color tuning in PF via excitation energy transfer onto perylene dyes fragments introduced as (i) randomly distributed co-monomer in the PF chain, (ii) end-capping group or (iii) side chain.⁴¹⁷ Perylene compounds are known for their high stability, great Q.E. and large range of emission colors, achieved via introducing different substituents. The random co-polymers (**Comp. 347–Comp. 353**) have been synthesized by Yamamoto coupling of dibromodialkylfluorenes with corresponding brominated perylenes (1–5%). The M_n in the range of 30,000–140,000 (90–400 units in a chain) and very high polydispersity (4.1–7.7) observed in these polymers were explained by relatively low reactivity of bromoperylene co-monomers. The photoluminescence spectra of the prepared co-polymers in solution were essentially identical to those of PF homopolymers, while in the solid state an efficient energy transfer onto dyes fragments occurred, giving rise to an additional red-shifted emission band, which position depends on the perylene structure. The energy transfer appears to be as efficient with 1% of the dye as with 5%. Generally, the PL efficiencies of the co-polymers in solid films varied from 38% to 56%, with exception of material **Comp. 351** having 3% of both of perylene fragments (which showed the PL efficiency of only 7%). The later was explained by aggregation of the perylene units in the solid state. The devices made from these co-polymers in configuration ITO/PEDOT/co-polymer/Ca showed stable emission color and external Q.E. of 0.2–0.6%, and the EL efficiency 0.9–1.6 cd/A, which are rather high as for non-optimized devices. In contrast to PL spectra, there was a complete energy transfer in the EL spectra (no fluorene emission), and the emission color can be finely tuned by structural modifications in perylene units (Table 2, **Figure 22**).

A very efficient energy transfer (producing emission at 613 nm) was observed in PL spectra of the perylene end-capped polymer **Comp. 353** in solid films. This material had the highest Q.E. (>60%) among the fluorene-perylene polymers, although the performance of its PLED has not been yet reported.⁴¹⁷

Attaching perylene moieties as side groups, allows achieving their high concentration without affecting the electronic structure of the polymer backbone. Putting 16% of the perylene moieties as side chains predictably results in more efficient energy transfer, which was observed in polymer **Comp. 352**, both in solution and solid state (emission band at 599 nm). Although no PLED device with **Comp. 352** has been reported yet, this material showed excellent performance in solar cells (external Q.E. 7%, in blend with PPV).⁴¹⁷

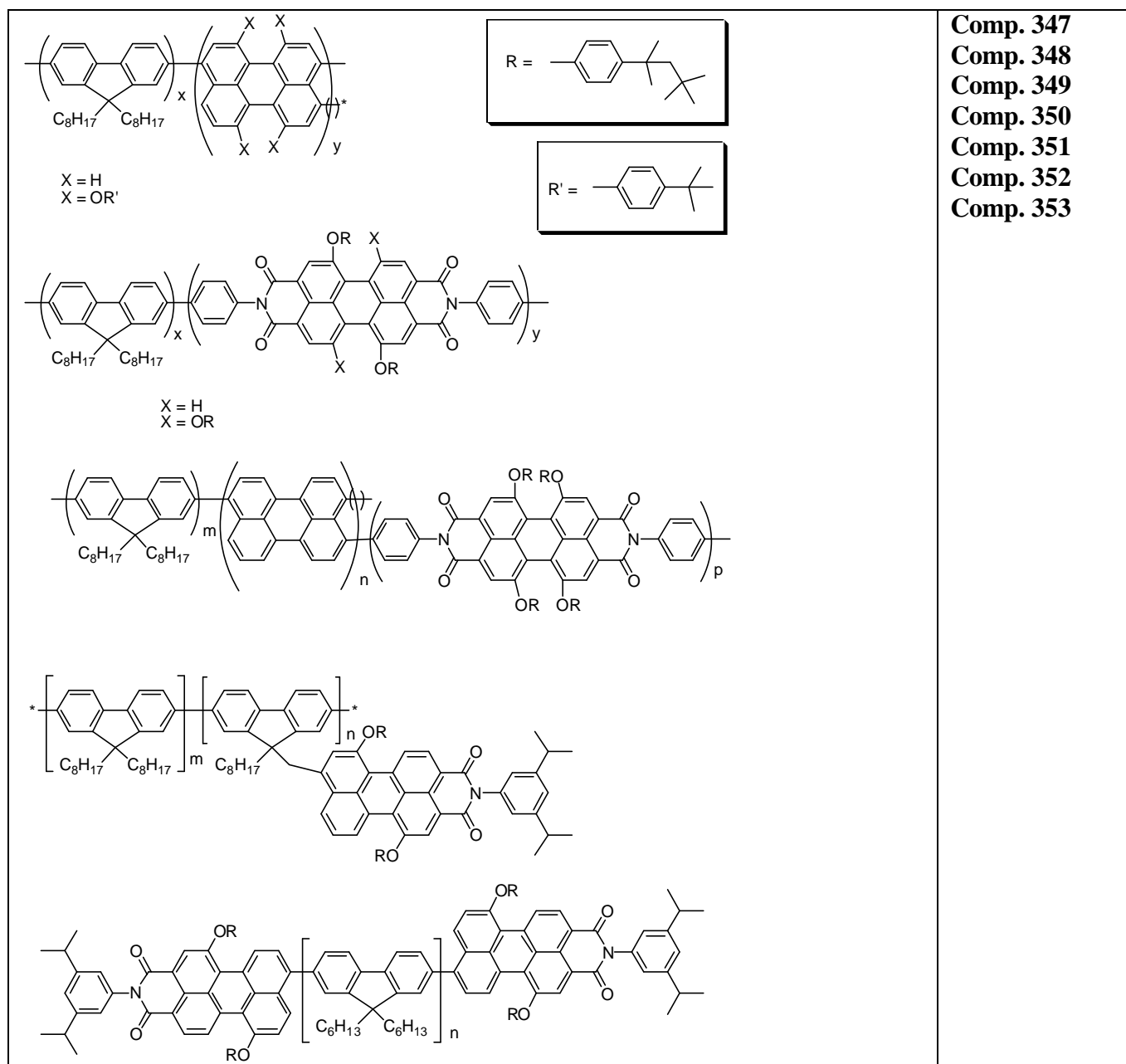


Table 2. Optical and electronic properties of the fluorene-perylene co-polymers.

Polymers (% dye) Emission Color	M_n , g/mol (PDI)	Φ_{PL} (film)	EL λ_{max} nm [Φ_{EL}^{ex}] CIE (x, y)	Turn-on voltage (V)	Luminous efficiency (cd/A)
Comp. 347 (3%) Bright Green	47,930 (4.1)	51 %	520 [0.6 %] (0.362, 0.555)	12	0.9
Comp. 348 (5%) Yellow	32,300 (4.9)	40 %	558 [0.2 %] (0.414, 0.519)	11	0.4
Comp. 349 (5%) Deep-red	63,510 (3.6)	33 %	675 [0.5 %] (0.636, 0.338)	8	1.6
Comp. 350 (1%) Red-orange	142,500 (3.8)	42 %	600 [0.3 %] (0.590, 0.365)	15	1.4

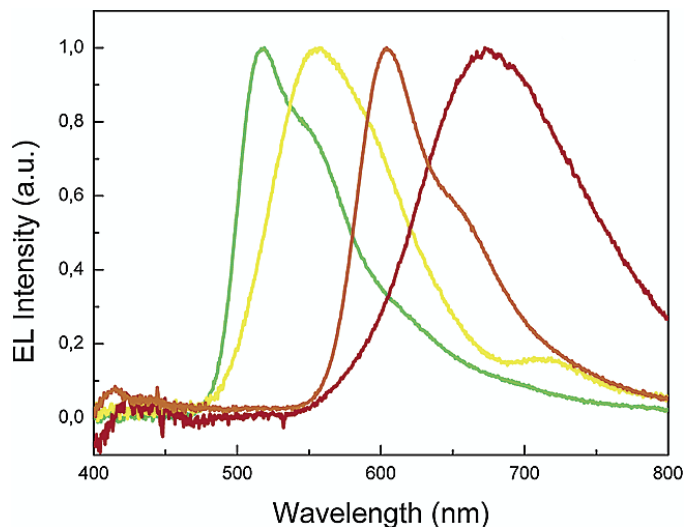
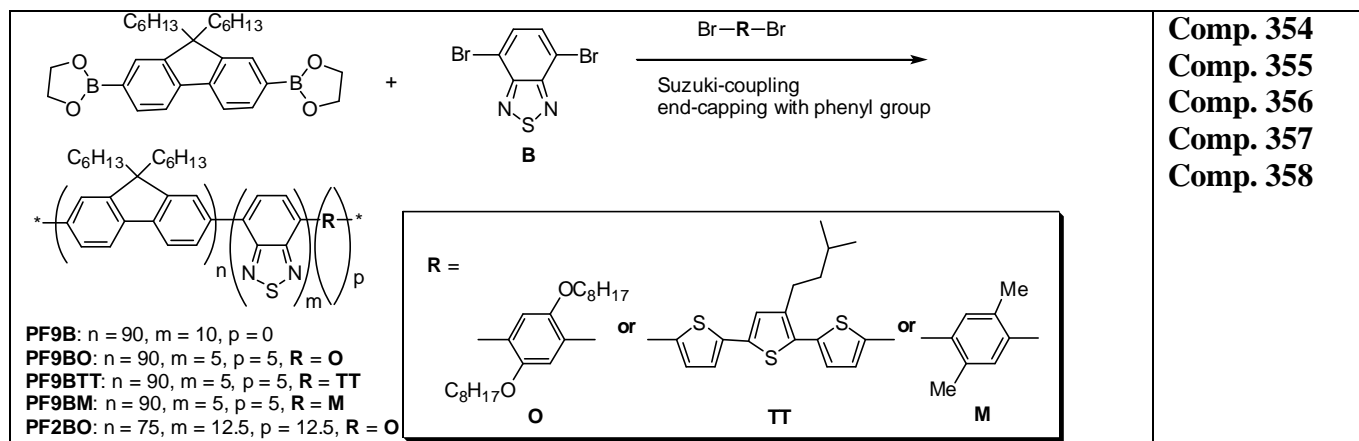


Figure 22. EL spectra of the co-polymers (from left to right) **Comp. 347**, **Comp. 348**, **Comp. 350** and **Comp. 349** in devices ITO/PEDOT/polymer/Ca/Al. [From Ref. 417, © 2003 American Chemical Society].

2.11.4. Co-polymers with three or more co-monomer units.

Alex Jen's group reported a series of highly efficient random conjugated co-polymers **Comp. 354–Comp. 358** containing dialkylfluorene and electron-deficient benzothiadiazole (BT) units, synthesized by Suzuki-coupling polymerization (Scheme 54).⁴¹⁸ To balance the charge transport and charge injection properties, a third, electron-rich unit was introduced in the polymer.



Scheme 54. Synthesis of fluorene/benzothiadiazole co-polymers.

All the co-polymers showed very similar absorption spectra ($\lambda_{\text{max}} = 380$ nm). The luminescence properties of the co-polymers are dominated by the BT unit: all the co-polymers have similar red-shifted luminescence peak at $\lambda_{\text{PL}} = 540$ nm ($\Phi_{\text{PL}} = 23\text{--}55\%$, depending on the monomer), and the third co-monomer does not contribute to the emission spectra. This can be explained by the charge transfer or energy transfer process between the electron rich segments and electron deficient BT units. Although the luminescence properties of the co-polymers are the same, their charge transport properties

are quite different. The authors studied current-voltage characteristics of metal-polymer-metal junctions, fabricated with metals of high and low work function. As expected, the highest hole conductivity belongs to terthiophene-contained polymer **Comp. 356** (for the price of the lowest electron conductivity). The highest electron conductivity was achieved in the polymer **Comp. 358**, having the highest ratio of electron deficient BT component. Remarkably, the last polymer showed the best performance in LED devices, which demonstrates that increasing the electron conductivity balances the charge-transport properties in PF materials. The PLEDs were fabricated in configuration ITO/HTL/Co-polymer/Ca, (HTL was either PEDOT or BTPD-PFCB, **Comp. 130**). The lowest performance was revealed by co-polymer **Comp. 356**, and attributed to the oligothiophene unit quenching effect. The best device, fabricated in configuration ITO/BTPD-PFCB/**Comp. 358**/Ca/Al, had an external Q.E. of remarkable 6.0 % and the photometric power efficiency of 18.5 cd/A (even higher efficiency of 28.6 cd/A for a unspecified device structure is reported in conclusions⁴¹⁸). The highest brightness of 59,400 cd/m² was achieved in this device at 15.2 V. Interestingly, when the PEDOT was used in same device structure instead of BTPD-PFCB, the PLED performance was essentially lower: the external Q.E. of 1.5%, EL current efficiency of 4.66 cd/A and the maximal brightness of 21,000 cd/m². However, as seen from the Figure 23, the higher performance of HTL **Comp. 130** only reveals at relatively high voltage (>12 V), and thus cannot be taken as a general rule for all PLEDs.

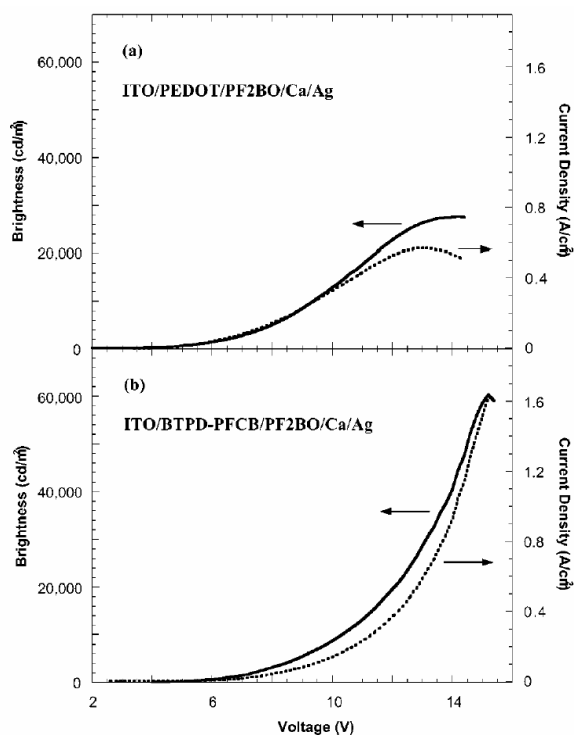
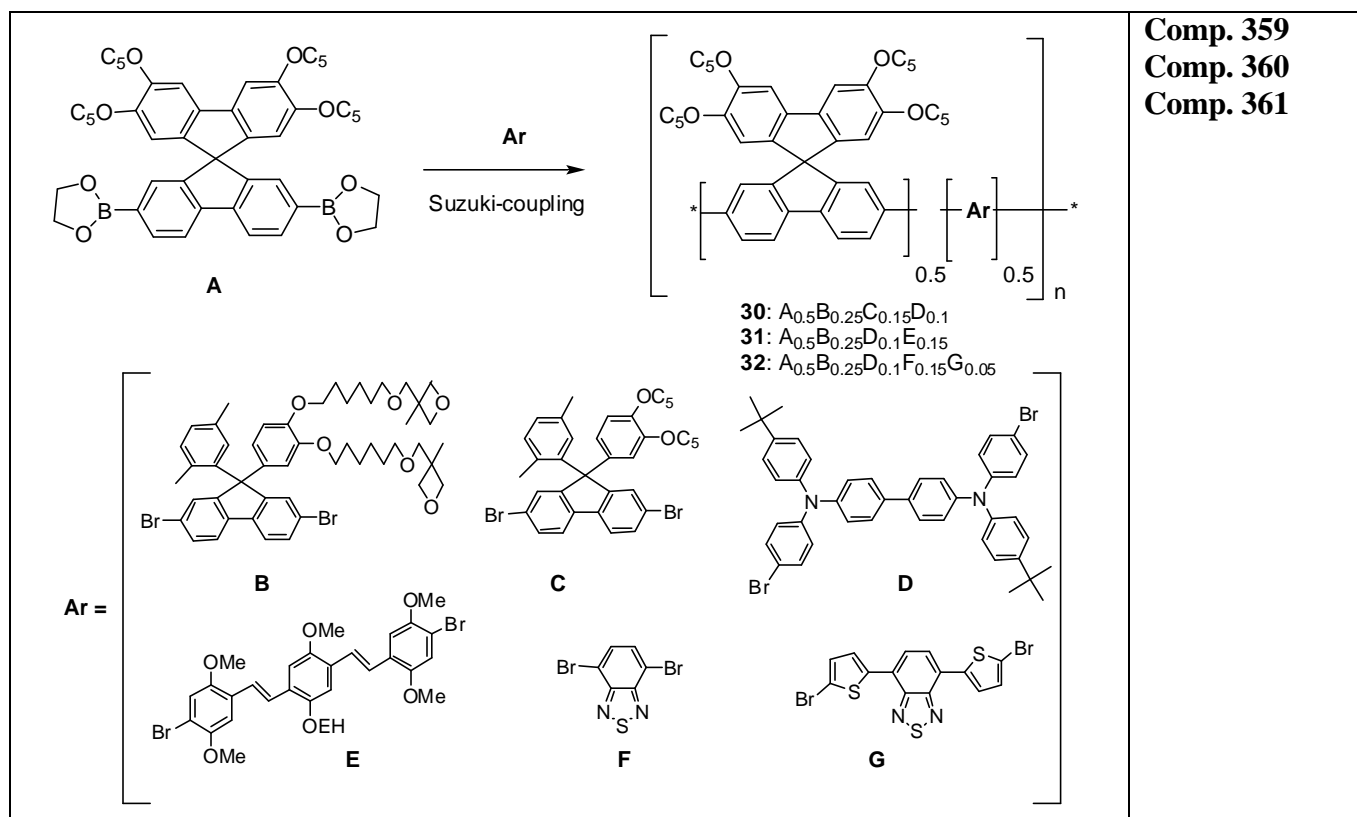


Figure 23. The plot of brightness (-) and current density (...) vs. applied voltage for PLEDs (a) ITO/PEDOT/**Comp. 358**/Ca/Ag and (b) ITO/**Comp. 130**/**Comp. 358**/Ca/Ag. [From Ref. 418, © 2000 American Chemical Society].

A further development of the approach of using multicomponent PF co-polymers for tuning the emission color was recently exemplified by fabrication of RGB prototype display, in which the pure red, green and blue colors was achieved by simple variation of the feed ratio of several monomers (Scheme 55).⁴¹⁹ The resulting polymers were very soluble in organic solvents, had usual for Suzuki

coupling high molecular weight ($M_n \sim 50,000$), and revealed a very respectful EL performance. The PLED fabricated as ITO/PEDOT/Polymer/Ca/Al showed switch-on voltages of 4.5 V for blue emitter **Comp. 359**, 3.8 V for green-emitter **Comp. 360** and 7.5 V for red-emitted **Comp. 361**, and maximal EL efficiency of 3.0, 6.5 and 1.1 cd/A, respectively. The presence of a photo-polymerizable (in the presence of photoacid) oxetane unit in the co-monomer B renders insoluble cross-linked polymer upon photolithographic development and allowed solution-process fabrication of the PLED display bearing different emitting materials.



Scheme 55. Suzuki synthesis of multicomponent co-polymers for RGB PLED display.⁴¹⁹

Table 3. Thermal and optical properties of PFs.

Polymer	M_n , g/mol (PDI)	T_g / °C	T_{dec} / °C	λ_{max}^{abs} / nm {solution}	λ_{max}^{abs} / nm {film}	λ_{max}^{PL} / nm {solution} ^a [Φ_f / %]	λ_{max}^{PL} / nm {film} ^a [Φ_f / %]	E_g / eV	Ref.
Comp. 187	35,700 (2.3)	75 ^c	421	385 (p-xylene)	391	415 [82 %]	425	2.91	316
Comp. 187	24,300 (1.4)	103	390	379	385.5	415 (438, 469) [82 %]	422 (444, 476) [74 %]	2.86	420
Comp. 193	5,600 (1.6)	130	407	374 (CHCl ₃)	366	412 (436) [48 %]	430		299
Comp. 194	41,200 (4.3)	128	412	388 (CHCl ₃)	380	420 (445) [93 %]	434		299
Comp. 197	20,700 (1.75)			389 (THF)			417 (439, 473)		268

Comp. 205	35,000 (1.9)	90	351	392 (THF)	394	419 (443) [92 %]	424 (448) [26 %]		312
Comp. 206	18,000 (2.2)	59	371	388 (THF)	392	418 (442) [99 %]	424 (448) [58 %]		312
Comp. 207	15,000 (2.5)	56	360	380 (THF)	385	417 (439) [100 %]	423 (446) [75 %]		312
Comp. 215	34,000 (2.2)	106	425	385 (p-xylene)	392	415 [82 %]	425	2.91	316
Comp. 216	77,000 (2.4)	110	427	386 (p-xylene)	391	415 [83 %]	424	2.91	316
Comp. 218	7,000 (1.8)			382 (THF)		410 (436), 538 (THF)	572		320
Comp. 219	13,500 (1.8)			382 (THF)		410 (436)			320
Comp. 258	12,000 (2.28)	150		394 (372) (DCM)		402 (426) 73 %] (DCM)			351
Comp. 259	25,100 (2.50)	114		396 (380) (DCM)		420 (442) 9[75 %] (DCM)			351
Comp. 260	30,400 (2.70)	98		395 (381) (DCM)		422 (443) [72 %] (DCM)			351
Comp. 261	21,600 (2.63)	127		396 (379) (DCM)		422 (444) [67 %] (DCM)			351
Comp. 277	19,500 (1.9)				360		428, 445 [44%]	2.97	362
Comp. 280	35,200 (1.57)			385 (THF)	383	413 (435) (THF)	453, 477 (425)	2.88	366
Comp. 281	37,200 (1.49)			424, 448 (THF)	432, 459	463 (492) (THF)	521	2.52	366
Comp. 282	59,200 (1.92)			392, 409 (THF)	395, 425	424 (444) (THF)	477, 503 (439)	2.74	366
Comp. 321	23,500 (1.52)	186	407		352, 457		662, 712 [7 %]	2.22	395
Comp. 322	24,200 (1.58)	119	406		345, 435		641, 704 [5 %]	2.32	395
Comp. 323	20,700 (1.61)	73	406		347, 438		641, 705 [4 %]	2.30	395
Comp. 354	87,900 (1.7)	115			377 (438)		542 (561) [46 %]		418

^a The data in the parentheses are the wavelengths of shoulders and subpeaks. ^b E_g stands for the bandgap energy estimated from the onset wavelength of the optical absorption. ^c From Ref. 358.

Table 4. Electrochemical properties of PFs.

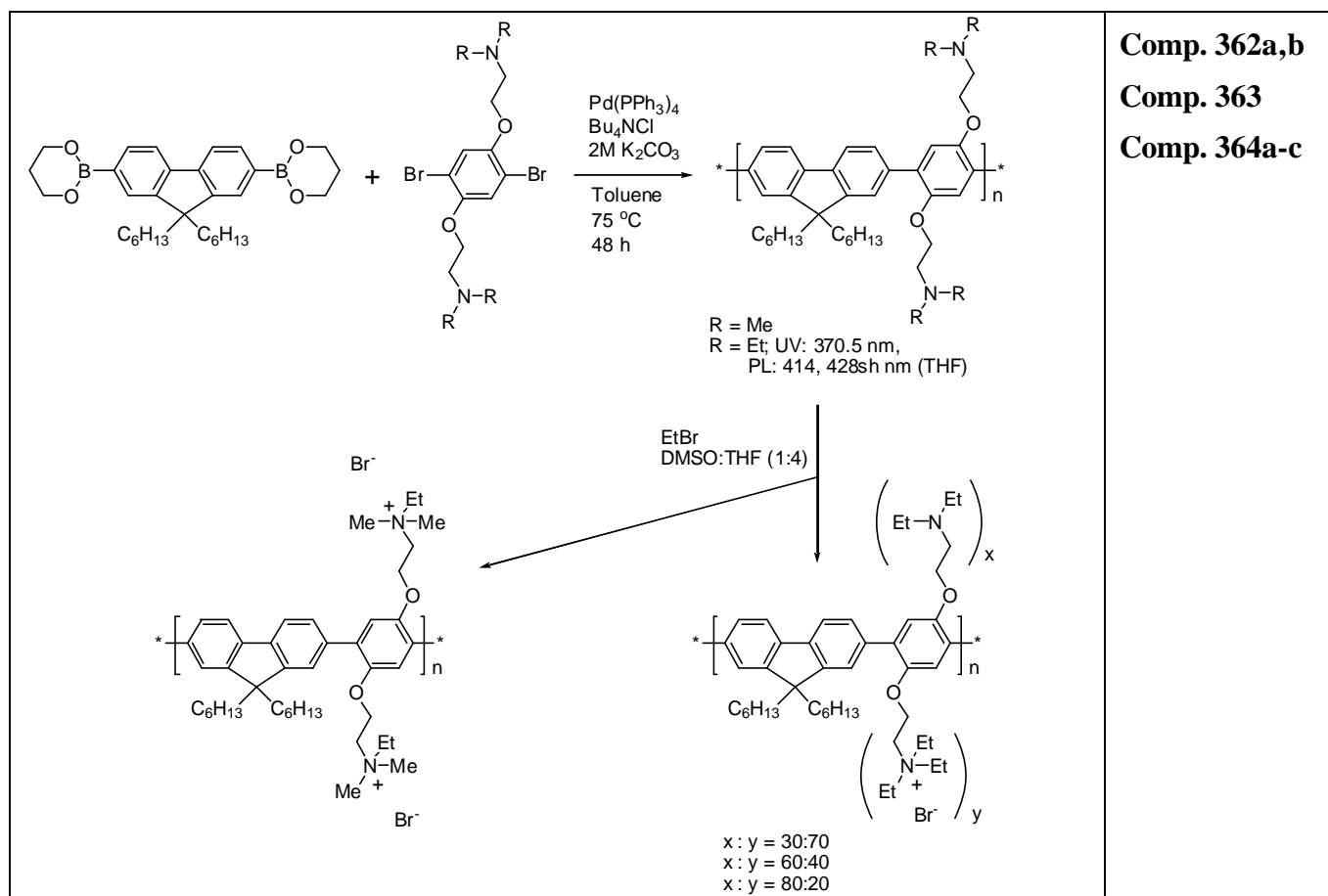
Polymer	$E^{(n)} /$	$E^{(p)} /$	$E_g /$ eV	HOMO / eV	LUMO / eV				Ref.
---------	-------------	-------------	------------	-----------	-----------	--	--	--	------

	V^a	V^a							
Comp. 187	-2.03	1.10	3.13	-5.50	-2.37				420
Comp. 193	-2.02	1.25	3.27	-5.65	-2.38				299
Comp. 194	-2.10	1.28	3.37	-5.67	-2.30				299
Comp. 280	-1.76 (SCE)	1.39	3.25						366
Comp. 281	-1.60 (SCE)	1.01	2.61						366
Comp. 282	-1.67 (SCE)	1.50	3.17						366
Comp. 321	-0.83	1.38	2.21	-5.78	-3.57				395
Comp. 322	-0.86	1.39	2.25	-5.79	-3.54				395
Comp. 323	-0.87	1.37	2.24	-5.77	-3.53				395
Comp. 354				-5.68	-3.67				418

^a The data in the parentheses are the wavelengths of shoulders and subpeaks. ^b E_g stands for the bandgap energy estimated from the onset wavelength of the optical absorption,

2.12. Polyfluorene-based polyelectrolytes.

Fluorene-[2,5-di(aminoethoxy)benzene] co-polymers **Comp. 362a,b** have been synthesized by Huang et al. as precursors to the first water-soluble cationic PFs **Comp. 363**, **Comp. 364a-c** (Scheme 56).^{421,422}

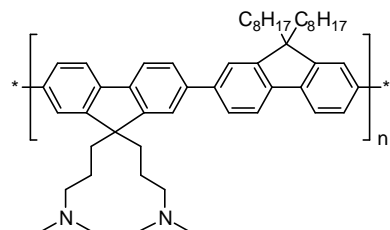


Scheme 56. Synthesis of water-soluble blue-emitting fluorene co-polymers.

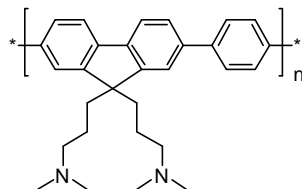
Whereas the neutral polymers **Comp. 362a,b** readily dissolve in common organic solvents, such as THF, chloroform, toluene, and xylene (but not in DMSO, methanol or water), their quaternization produces material **Comp. 363** which is insoluble in chloroform or THF, but completely soluble in DMSO, methanol, and water. For co-polymers **Comp. 364a-c** with partial degree of quaternization the solubility is intermediate between the neutral and fully quaternized polymers. Whereas neutral polymers **Comp. 362a,b** showed good thermal stability ($T_{\text{dec}} = 400$ and 340 °C, respectively, in nitrogen), quaternized polymers **Comp. 363** and **Comp. 364a-c** begin to decompose at *ca.* 230 °C⁴²² although a higher value of $T_{\text{dec}} = 300$ °C was reported in preliminary communication.⁴²¹ Both neutral and quaternized polymers absorb and emit in the region typical for polyfluorenes with only small variations (~ 10 nm) in PL depending on the structure and the solvent, e.g. **Comp. 362a**: $\lambda_{\text{abs}} = 370.5$ nm, $\lambda_{\text{PL}} = 414, 428 \text{ sh nm}$ (THF); **Comp. 364a-c**: $\lambda_{\text{abs}} = 360.5$ nm, $\lambda_{\text{PL}} = 410$ nm (methanol). Φ_{PL} in solutions is very high for both neutral [**Comp. 362a**: 87 % (CHCl_3); **Comp. 362b**: 57 % (THF)] and quaternized [**Comp. 363**: 76 % (methanol), 25 % (H_2O)] polymers. The decrease of Φ_{PL} for **Comp. 363** in water was attributed to the aggregation, and further decrease in Φ_{PL} for this polymer was observed in films (4 %). No EL devices with these co-polymers were reported.

A series of fluorene co-polymers with amino-functionalized side chains **Comp. 365** and **Comp. 366** have been prepared by the same group. After quaternization they gave co-polymers **Comp. 367** and **Comp. 368** which are soluble in polar solvents (methanol, DMF, DMSO).⁴²³ Devices from the neutral co-polymers **Comp. 365** and **Comp. 366** and the quaternized co-polymers **Comp. 367** and **Comp. 368** showed similar absorption and PL spectra but very different EL spectra. For the neutral

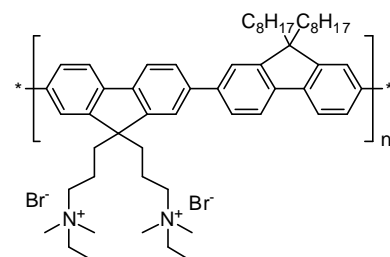
polymers high energy peaks observed in PL spectra is displaced with a new broad low energy peak. In the same time, main peaks in the EL spectra of quaternized co-polymers coincide well with PL emission, with only one additional shoulder around at 492–497 nm, which authors assigned to excimer emission. Using **Comp. 365** as electron injection layer in ITO/PEDOT/MEH-PPV/**Comp. 365**/Al configuration gave the devices with luminance of 3,000 cd/m² and external Q.E. of 2.3 %.



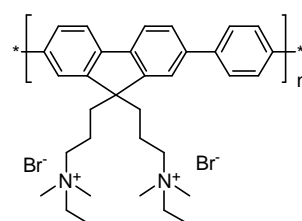
UV: 390 nm, PL: 425, 449 nm, EL: 515 nm



UV: 382 nm, PL: 420, 444 nm, EL: 535 nm



UV: 400 nm, PL: 431, 455 nm, EL: 433, 492 nm



UV: 388 nm, PL: 425, 447 nm, EL: 442, 497 nm

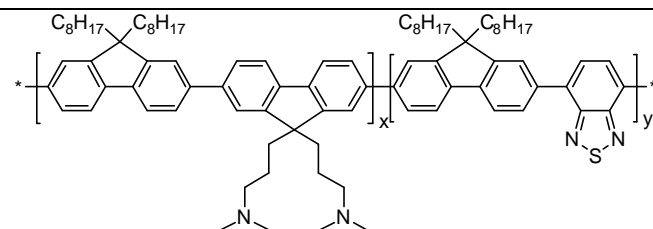
Comp. 365

Comp. 366

Comp. 367

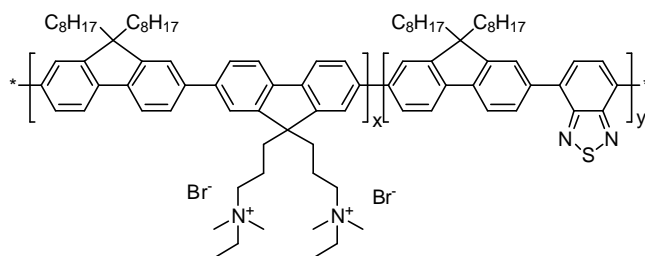
Comp. 368

When electron deficient benzothiadiazole unit was incorporated into backbone of such polymers, an efficient energy transfer results in complete quenching the fluorescence from the fluorene sites already at concentration of benzothiadiazole moieties as low as 1% (for both neutral and quaternized co-polymers, **Comp. 369** and **Comp. 370**).⁴²⁴ They emit green (544–550 nm, **Comp. 369**) to yellow (555–580 nm, **Comp. 370**) light and can be processed from environment-friendly solvents like alcohols. The PLED fabricated with these polymers showed high external Q.E. over 3% and 1% for **Comp. 369** and **Comp. 370**, respectively (with Al cathode).



x:y = 99.5:0.5
99:1
95:5
85:15

UV: 384-375 nm, PL: 544-550 nm, Q.E.(PL): 85-71 %

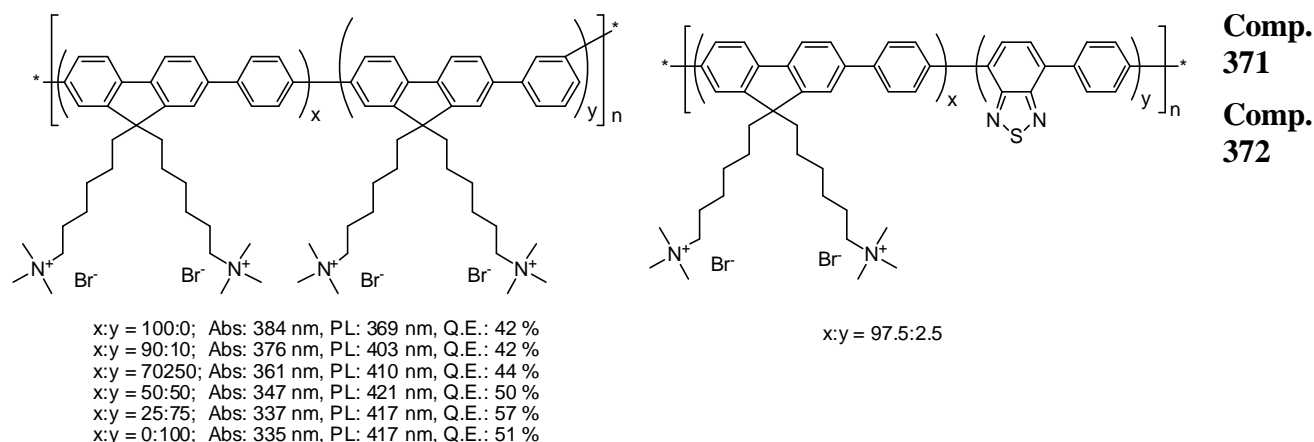


UV: 391-382 nm, PL: 555-580 nm, Q.E.(PL): 23-381 %

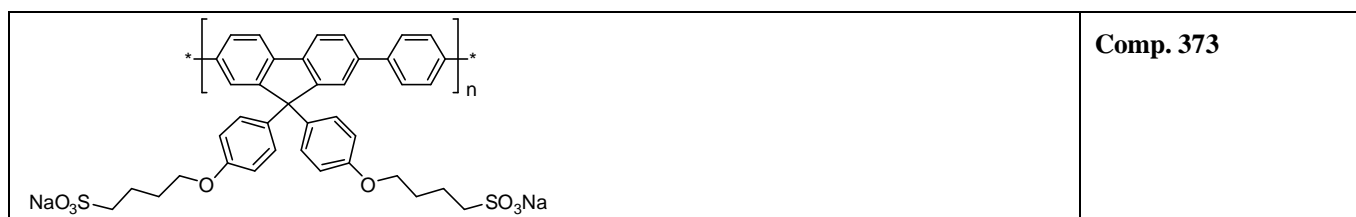
Comp. 369

Comp. 370

Bazan et al. reported similar water-soluble random cationic fluorene co-polymers **Comp. 371** and **Comp. 372** with quaternary ammonia side groups attached via C-9 position of the fluorene moiety.⁴²⁵ There was a progressive blue shift in absorption spectra of copolymers **Comp. 371** with increasing amount of *meta* linker in the polymer chain. In PL spectra, however, increasing the *para* content above 50:50 ratio did not perturb the emission maxima, which was assigned to localization of excitons on the longest conjugated segments. In deionized water, at concentrations below 10^{-6} M, absorption and emission spectra of copolymer **Comp. 372** are nearly identical to that of **Comp. 371**, which lacks benzothiadiazole units. Complexation of **Comp. 372** with oppositely charge polyelectrolytes (such as DNA) brings together polymer segments and encourages energy migration to low-energy emissive benzothiadiazole sites. Thus, when noncomplimentary ssDNA is present in solution, the PL maxima of **Comp. 372** is shifted to green ($\lambda_{PL} = 550$ nm) and to red ($\lambda_{PL} = 681$ nm) when the complimentary ssDNA is present. *[so what??? Why it is important for LEDs??? We are long at the stage where we need to cut the chapter, not to expand it with secondary details]*



Whereas all above water-soluble polyfluorenes are tetraalkylammonium-based cation electrolytes, Burrows et al. reported on anionic fluorene-based copolymer **Comp. 377**, which showed blue shift in PL (from 424 to 411 nm) and dramatic increase in the fluorescence quantum yield (from 10–15% to 60%) when incorporated into *n*-dodecylpentaerythritol ether micelles.⁴²⁶

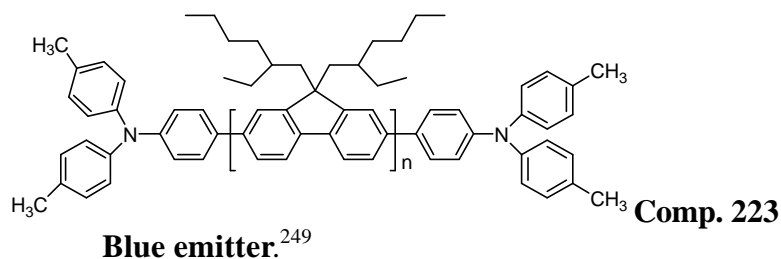


2.13. Conclusions.

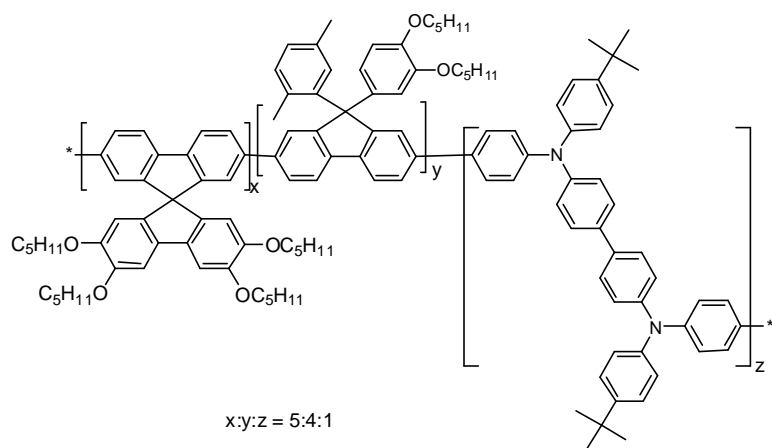
Clearly, at present PFs are the most promising class of blue-emitting materials. The original problem associated with undesirable “green emission band” was shown to be a result of exciton trapping on the electron deficient fluorenone defect sites. The color purity can be reestablished via a)

careful purification of the monomer (complete elimination of mono-substituted units), b) inserting a protecting layer between the PF and reactive cathode material, c) introducing hole-trapping sites (most commonly, triarylamine units), which would compete with fluorenone defects, minimizing the excitone formation on the latter, d) introducing bulky substituents into PF backbone, which would minimize the exciton trapping on fluorenone defects. Furthermore, introducing of different conjugated moieties into PF backbone allows for efficient color tuning in these materials.

So far, the most efficient PLED based on PFs in terms of pure red, green and blue emission can be summarized in the following examples.

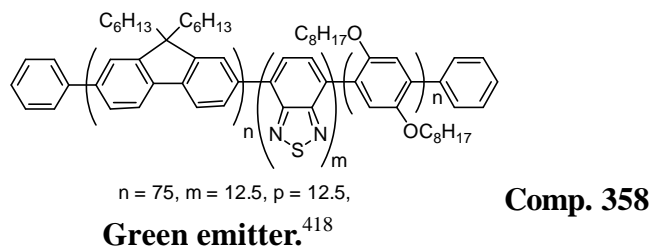


A single layer device ITO/PEDOT/**Comp. 223**/Ca can be turned on at 3.5V, emits blue light (CIE: $x = 0.150$, $y = 0.080$) with EL efficiency of 1.1 cd/A (at 8.5 V; power efficiency of 0.40 lm/W) and maximal brightness of 1,600 cd/m². A multilayer device with a structured triarylamine-based HTL allows to achieve the EL efficiency of over 2.7 cd/A and higher (maximal brightness of 5,000 cd/m²).

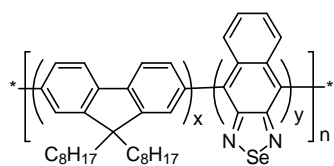


Blue emitter.⁴¹⁹

A single layer PLED ITO/PEDOT/Comp. 374/Ca emits blue light (CIE: $x = 0.15$, $y = 0.16$) with current efficiency of 3.0 cd/A and operating voltage of 4.6 V (at 100 cd/m²).



The device with configuration structure of ITO/BTPD-PFCB/**Comp. 358**/Ca/Ag works at operating voltage of 3.6 V and allows to rich large external Q.E. efficiency 6 % (18.9 cd/A) and a maximum brightness of 59,400 cd/m².



x : y = 99:1

Comp. 342

Red emitter. ⁴¹¹

A single layer PLED ITO/PEDOT/polymer/Ba operates at 8.9 V, emitting saturated red color (CIE: x = 0.67, y = 0.33) with very high external Q.E. of 3.1%, which correspond to photometric current efficiency of 0.9 cd/A. The brightness in excess of 2,000 cd/m² was achieved for this device.

3. Polythiophenes (PTs)

Polythiophenes (PTs) (including oligothiophenes) are one of the most studied and important classes of linear conjugated polymers.^{427,428} Versatile synthetic approaches to PTs, both chemical⁴²⁹ and electrochemical,⁴³⁰ easy functionalization and unique electronic properties, which can be widely tuned, focus a tremendous interest to this class of polymers.

Due to electron-rich character of the thiophene ring, PTs can be easily and reversibly oxidized by chemical or electrochemical mean to form p-doped, usually highly conducting materials. The first electronic transition of undoped PT (which strongly depends on the structure) lies between 300 and 500 nm ($\epsilon \sim 10,000 \text{ M}^{-1} \text{ cm}^{-1}$),⁴³¹ upon doping undergoes dramatic bathochromic shift transforming into so-called “conducting” band, which tails from the visible to deep IR region. In contrast to undoped PTs, which exhibit reasonably strong luminescence in the visible region of the spectrum, the doped PTs are not luminescent, although partially doped PTs have been used in light-emitting electrochemical cells (LECs) (see section 3.4.) and doped PEDOT is routinely used as an electrode for PLED (mostly as a second layer on ITO-covered glass).

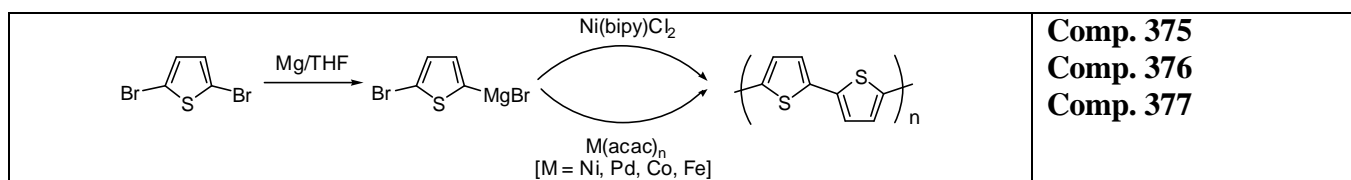
Although in sense of electroluminescent materials, PTs have not been studied as widely as PPVs or polyfluorenes, yet they present an important class of LEP. PTs can show good red emission, consistent with their bandgap of *ca.* 2 eV, a color, which is difficult to produce with other LEP. Often the luminescence efficiency of PTs in the solid state is relatively low,^{432,433} much lower than that of PPV and polyfluorenes, which originates from their solid state structure – a tendency of strong interchain interactions (especially for low molecular weight oligomers). This feature is an advantage of PTs in some electronic applications as, e.g., field-effect transistors.⁴³⁴ However, it becomes one of the most critical drawbacks for application as emissive materials in LED. Whereas in solution the photoluminescence efficiency (Φ_{PL}) of poly(3-alkylthiophenes) is ~30–40 %, it drastically drops down to 1–4 % and lower in the solid state, due to increased contribution of nonradiative decay via interchain interactions and intersystem crossing caused by the heavy-atom effect of sulfur.⁴³⁵ Thiophene-based polymers have stronger spin-orbital coupling than phenylene-based polymers due to the internal heavy atom effect of the sulfur heteroatom and hence triplet state processes play a greater role in their photophysics.⁴³⁶

Another feature of PTs is the phenomenon of thermochromism,⁴³⁷ which has been shown for poly(3-alkyl)thiophenes in many publications. It is believed that the thermochromism observed in poly(3-alkyl)thiophene films originates from the thermal movement of the side chains, shifting a predominantly planar structure of chains at low temperatures to a random coil conformation when the temperature is increased, thus forcing the polymer backbone out of planarity. This leads to decrease of orbital overlap and effective conjugation length, resulting in increase of the bandgap and blue shift in the polymer absorbance (from red to purple or purple-blue).^{438,439} The process is completely reversible and on cooling the initial color of the film is restored. Presenting a theoretical interest for understanding structural and electronic features of PTs, thermochromism, however, is undesirable for LED application, as it could lead to changes of the emission wavelength and the quantum efficiency of the device during the operation.

3.1. General Synthetic Routes to PTs

Polymerization of thiophenes can be carried out in many different ways and the most used methods can be generalized in three categories: (i) electropolymerization of the monomer, (ii) metal-catalyzed coupling reactions, and (iii) chemical oxidative polymerization. Electropolymerization is a

widely used method to prepare insoluble films of PTs and present a simple and efficient way to study optical and electronic properties of PTs,⁴³⁰ although it is rarely used in preparation of electroluminescent materials. In 1980 Yamamoto et al. reported on Ni-catalyzed polycondensation of 2,5-dibromothiophene **Comp. 375**, which first reacted with Mg in THF yielding 2-magnesiobromo-5-bromothiophene **Comp. 376** with further polymerization in the presence of Ni(bipy)Cl₂ yielding PT **Comp. 377** (Scheme 57).⁴⁴⁰ The same year Lin and Dudek described another example of metal-catalyzed route to unsubstituted PT **Comp. 377**, exploiting acetylacetonates of Ni, Pd, Co or Fe as catalysts.⁴⁴¹



Scheme 57. Synthesis of polythiophene via metal-catalyzed couplings.

PT synthesized by these methods has low molecular weight, because even at low molecular weights the material is insoluble and precipitates from THF; moreover, the elemental analysis indicates on the presence of 1–3 % of Mg. [ref] Later Ni(dppp)Cl₂ catalyst was exploited for polycondensation polymerization of bromo(iodo)-Grignard reagents of type **Comp. 376**.⁴⁴² Another polycondensation approach to PT, also reported by Yamamoto,⁴⁴³ included heating of **Comp. 375** with Ni(cod)₂ and triphenylphosphine in DMF at 60–80 °C. Due to very high yield (near quantitative) this reaction has been applied in syntheses of a wide range of conjugated polymers.

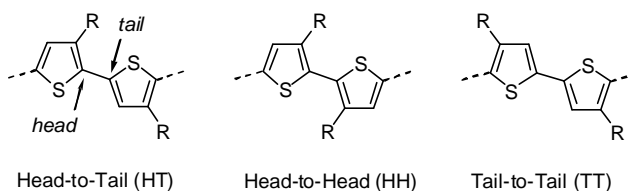
FeCl₃-Promoted polymerization of thiophene with in chloroform was described 20 years ago⁴⁴⁴ and currently presents the most widely exploited oxidative route to 3(3,4)-substituted PTs (Scheme 58). It gives rather high molecular weight polymers (often from $M_w = 20,000$ to 400,000) with polydispersity from 1.3 to 5.^{445,446} Other oxidative agents (e.g., ammonium persulfate) are of limited use, although oxidative coupling with CuCl₂ is widely used as a dimerization reaction of lithiothiophenes in syntheses of oligothiophenes.



Scheme 58. Synthesis of polythiophene via chemical oxidation polymerization.

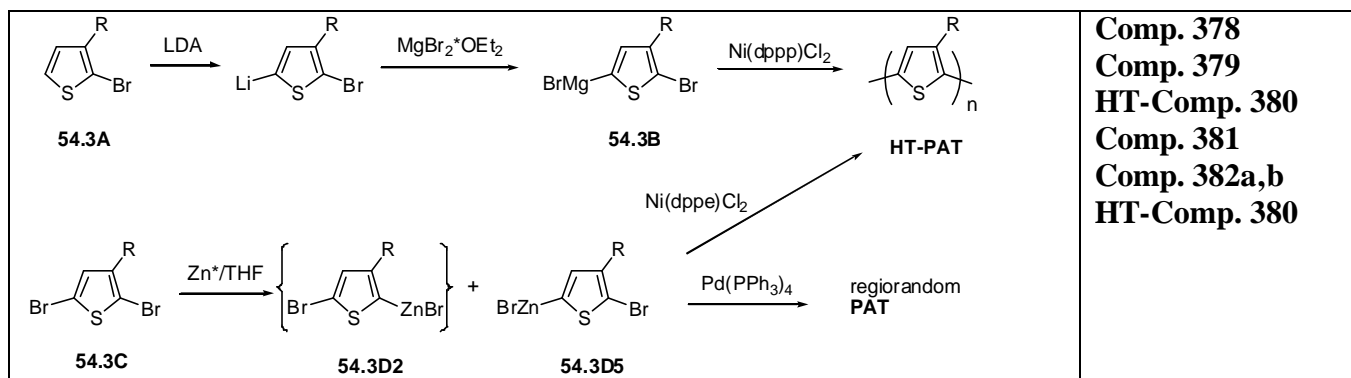
As already mentioned, unsubstituted polythiophene is an insoluble and infusible material. Once the polymer is prepared it is difficult (if not impossible) to further process it as a material for electronic applications. The solubility can be greatly enhanced by introduction of side chains at position 3 (or at both, 3 and 4). The most widely studied side chains are n-alkyl substituents, which can be easily introduced into the thiophene core by reaction of 3-bromothiophene with Grignard reagents from alkyl halides.⁴⁴⁷

While 3-substitution efficiently improves the solubility and the processability of the PTs, polymerization of 3-R-thiophenes can result in three different types of coupling of the thiophene rings along the polymer main chain, *i.e.* head-to-tail (HT), head-to-head (HH), and tail-to-tail (TT).



Generally, both oxidative polymerization and metal-catalyzed polycondensation afford all three possible types of isomers, *i.e.* HH, HT and TT, although this process is not completely random and electronic and steric factors have an influence on somewhat preferred HT coupling, which could reach more than 80–94%.^{448,449} Amou et al. showed that the regioregularity of FeCl₃-synthesized P3HT **Comp. 387** depends on the temperature of the reaction and the concentration, and in diluted solutions at –45 °C the regioregularity of P3HT approaches 90%.⁴⁴⁸

Several approaches leading to selective formation of the least sterically hindered HT-regioregular PTs have been developed in the last decade. The McCullough method presents the first synthesis of regioregular head-to-tail poly(alkyl)thiophenes (HT-PATs, **HT-Comp. 380**) (yielding almost 100% HT-coupling (Scheme 59).^{450,451} It is based on regiospecific metallation of 2-bromo-3-R-thiophene (**Comp. 378**) with LDA at position 5 and its further transformation into Grignard derivative **Comp. 379**. The latter is polymerized with catalytic amounts of Ni(dppp)Cl₂ using the Kumada cross-coupling method. The important modification of this synthetic route replaces the lithiation reaction by treatment the dibromothiophene derivative with methylmagnesium or vinylmagnesium bromide which affords the Grignard intermediate in one step.^{452,453,454} Other methods for preparing regioregular PTs exploiting Stille⁴⁵⁵ or Suzuki⁴⁵⁶ coupling instead of Grignard reagents have also been developed. Rieke has used highly reactive "Rieke zinc" (Zn*), which at low temperature reacts with 2,5-dibromo-3-R-thiophenes (**Comp. 381**) giving predominantly a 5-metallated compound (**Comp. 382a,b**), which is polymerized with a special bidentate catalyst Ni(dppe)Cl₂ yielding HT-regioregular PATs **HT-Comp. 380** (in contrast, use of monodentate Pd(PPh₃)₄, catalyst yields regiorandom PATs **HT-Comp. 380** in the same conditions).^{457,458} The detailed aspects of synthesis and characterization of regioregular PTs have recently been reviewed by McCullough.⁴²⁹



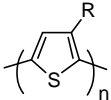
Scheme 59. McCullough and Rieke methods of synthesis of regioregular HT-poly(3-alkylthiophenes) **HT-Comp. 380**.

The presence of HH coupling in irregular PTs causes an increased twist of thiophene units (due to steric repulsion) and loss of conjugation. This results in increased bandgap (blue shift in an absorption and luminescence), decreased conductivity and other undesirable changes in electronic properties. As it will be shown below, regioregularity plays also an important role in luminescence properties of PTs and is used as a tool to tune the properties of PT-based LEDs.

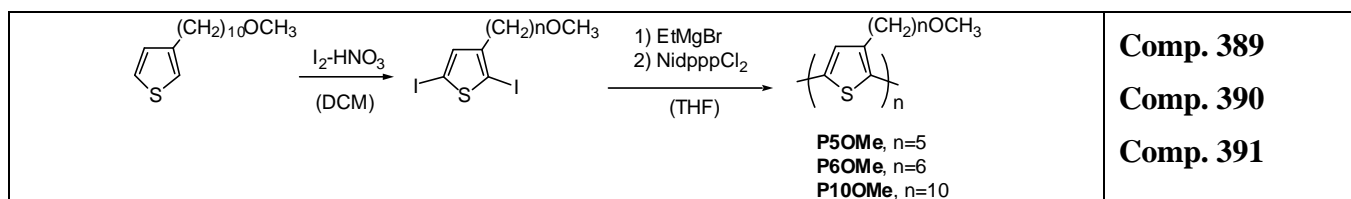
3.2. Light-emitting Thiophene Homopolymers.

3.2.1 PTs red light emitters.

Polythiophene LEDs were first reported by Ohmori et al. in 1991,^{459,460} who described poly(3-alkylthiophenes) **Comp. 383–Comp. 385** (prepared by oxidation of 3-alkylthiophenes with FeCl_3 in chloroform⁴⁴⁴) as red-orange emitting material (peak emission at 640 nm for **Comp. 383**) in single-layer ITO/**Comp. 383–Comp. 385**/Mg:In devices. It was particularly shown that the luminescence efficiency shows a linear dependence on the length of the alkyl chain, showing *ca.* four times increased EL efficiency for PT with $\text{R} = \text{C}_{22}\text{H}_{45}$ as compared to $\text{R} = \text{C}_{12}\text{H}_{25}$ (although no quantum yield values have been given in those reports), possibly owing to the improved confinement of excitons on a main chain with an increase of the side chain length.⁴⁶¹ Thus, the use of carrier confining layer (TPD) was shown to markedly increase (by 3–5 times) the device efficiency.⁴⁶⁰ Shortly afterwards Heeger's group reported on EL in poly(3-octylthiophene) **Comp. 386**, which showed red-orange luminescence with an external Q.E. at room temperature of 0.025 % in ITO/**Comp. 386**/Ca configuration.⁴⁶² Greenham et al. studying the EL from PTs **Comp. 385** and **Comp. 387** (also prepared by oxidation of the monomers with FeCl_3) achieved significantly higher emission efficiency of 0.2 % for **Comp. 385**, also using Ca as a cathode (**Comp. 387** gave 0.05 % with the same electrode, and use of Al cathode gave 0.01 and 0.003 %, respectively).⁴⁶³

 <p>54.5a-e, $\text{R} = \text{C}_{22}\text{H}_{45}(\text{a}), \text{C}_{18}\text{H}_{37}(\text{b}), \text{C}_{12}\text{H}_{25}(\text{c}),$ $\text{C}_8\text{H}_{17}(\text{d}), \text{C}_6\text{H}_{13}(\text{e}), \text{C}_{10}\text{H}_{21}(\text{g})$</p>	<p>Comp. 383 Comp. 384 Comp. 385 Comp. 386 Comp. 387 Comp. 388</p>
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Bolognesi et al. synthesized a modified poly(3-alkylthiophene) **Comp. 389–Comp. 391**,^{464,465,466} containing a methoxy group at the end of the alkyl chain by Ni-catalyzed polymerization of the corresponding 2,5-diiodothiophene (Scheme 60):

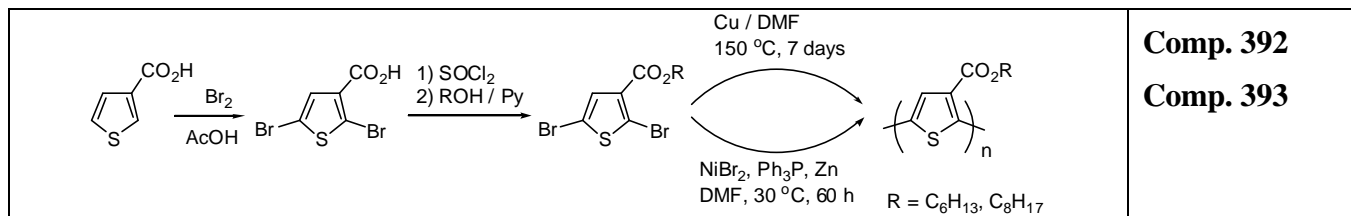


Scheme 60. Synthesis of alkylthiophenes **Comp. 389–Comp. 391** through oxidative iodination of the thiophene followed by Ni-catalyzed polymerization.

Small shifts in EL of polymer **Comp. 391** to higher energies as compared to polymer **Comp. 386** (from 1.8 eV to 1.95 eV) was mentioned,^{462,464} although it could be a result of asymmetry of the rather wide band (comparison with P3DT **Comp. 388** reveals a smaller blue shifts of 0.05 eV⁴⁶⁷). Polymers **Comp. 389** and **Comp. 390** showed high (for polythiophenes) PL quantum yields in solution (38–45% in THF), which, however, decreased in the films.⁴⁶⁶ A general explanation of this decrease as a result of the interchain interactions is supported by PL temperature dependence experiments: on gradual heating the sample to 140 °C the PL intensity was increased by ≈ 2 and ≈ 6 times, for **Comp. 389** and **Comp.**

390, respectively. The external Q.E. for **Comp. 389** and **Comp. 390** in ITO/Polymer/Al diodes are relatively low (10^{-5} – 10^{-4} and 5×10^{-3} %, respectively, at the same voltages).

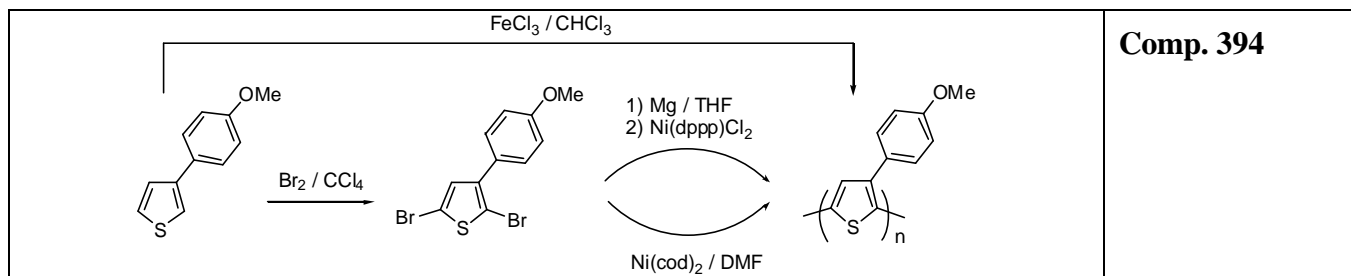
A larger blue shift in fluorescence was observed for alkoxy-carbonyl substituted PTs **Comp. 392** and **Comp. 393**. The polymers were prepared from 2,5-dibromosubstituted monomers by two methods: (i) Ullmann reaction with Cu powder and (ii) Ni(0)-mediated polymerization (Scheme 61).⁴⁶⁸



Scheme 61. Synthesis of alkoxy-carbonyl-PTs.

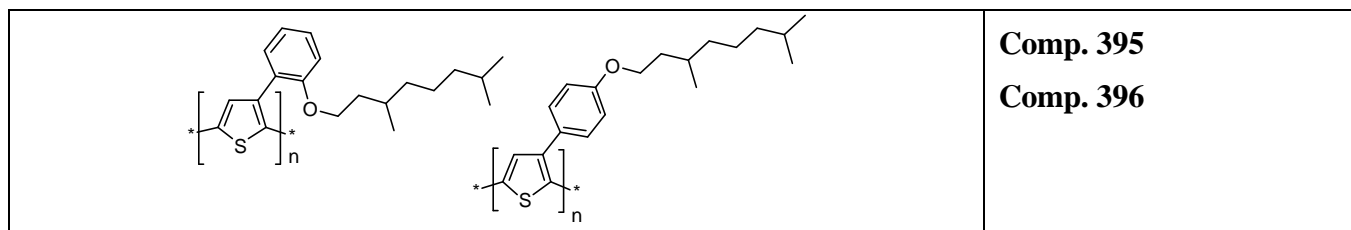
Both polymers have close molecular weights ($M_n \sim 3000$), although Cu-prepared polymers showed better quality and lower polydispersity. PL emission maxima for the Cu-prepared polymers **Comp. 392** and **Comp. 393** were red shifted as compared to Ni-prepared polymers [by 13–15 nm (≈ 0.05 – 0.06 eV) in solution and 25–30 nm (≈ 0.08 – 0.10 eV) in films, Table 1]. This demonstrates that the properties of the polymer depend on the preparation method, and, therefore, conclusions from small shifts of 0.05–0.1 eV in PL/EL energies of the materials prepared by different methods, should be made with care.

Another example of the effect of the polymerization method on the optical properties of the resulting polymer is the synthesis of polymer **Comp. 394** (Scheme 62).⁴⁶⁹ Polymers obtained by oxidative polymerization of corresponded 3-(methoxyphenyl)thiophene with FeCl_3 (CHCl_3 -soluble fraction), and with Mg / Ni(dppp)Cl_2 or Ni(cod)_2 polymerizations of corresponding dibromothiophene derivative showed somewhat different maxima in absorption (and PL emission) spectra: 405 (520), 433 (555), and 435 (560) nm, respectively.

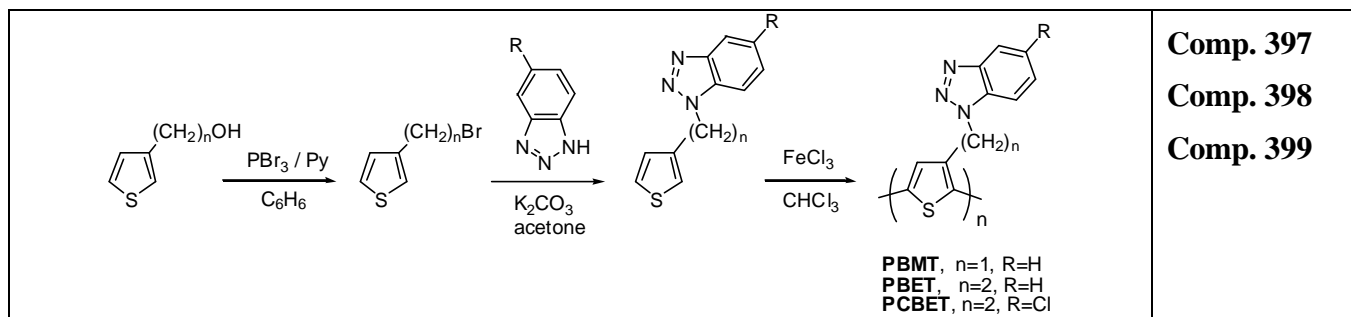


Scheme 62. Preparation of methoxyphenyl-PT **Comp. 394**.

Jin et al. synthesized and studied PL and EL properties of polymers **Comp. 395** and **Comp. 396**, which differ by the position of alkoxy-substituent in the phenyl ring, expecting different distortion of the polymer main chain (and consequently conjugation length) due to different steric factor for *para*- and *ortho*- substitution.⁴⁷⁰ Although absorption spectrum of the "*ortho*-polymer" **Comp. 395** showed substantial blue shift of 40 nm as compared to the "*para*-" **Comp. 396**, and decreased turn-on voltage of EL (4.5 and 6.5 V, respectively), both polymers demonstrated near the same PL and EL maxima (Table 1).



A series of PT derivatives (**Comp. 397–Comp. 399**) with electron transporting benzotriazole moieties in the side chains has been prepared (Scheme 63).⁴⁷¹



Scheme 63. Synthesis of triazole-containing PTs.

The polymer **Comp. 397** was insoluble in common organic solvents (THF, $CHCl_3$, or DMF). In contrast, polymers **Comp. 398** and **Comp. 399** with longer ethylene bridge between the polythiophene main chain and benzotriazole moiety possessed good solubility and high molecular weights and thermal stability ($T_{dec} > 300\text{ }^{\circ}C$). They showed pronounced blue shifts of 50–70 nm in absorption, PL and EL maxima, as compared to P3OT **Comp. 386** (Table 1), which was, somewhat speculatively attributed to steric hindrance.⁴⁷¹ The enhancement in EL efficiency of these polymers was not as dramatic as authors expected, although they showed 3–7 times higher Φ_{EL}^{ex} values. This was rationalized by considering the energy diagram (Figure 24): HOMO levels found from photoelectron spectroscopy, were -5.45 , -5.62 and -4.57 eV for **Comp. 398**, **Comp. 399** and P3OT (**Comp. 386**), respectively, and LUMO energy levels (estimated as E_{HOMO} plus optical bandgap from UV-Vis spectra) were correspondingly at -3.31 , -3.42 and -2.61 eV. Thus, both HOMO and LUMO levels of **Comp. 398** and **Comp. 399** were lowered by introducing the electron-withdrawing benzotriazole moiety, compared with those of P3OT **Comp. 386**. However, this strong effect is certainly due to replacing the alkoxy substituent with alkyl group, and not due to introduced triazole moiety, although the later might have contributed to the reduced LUMO. The authors note that the total barrier of charge injection was not reduced, although the enhancement of external EL efficiency was observed. It is not, however, surprising, in our opinion, because the balance between the hole and electron injection (which was improved significantly!), rather than total barrier determines the EL efficiency.

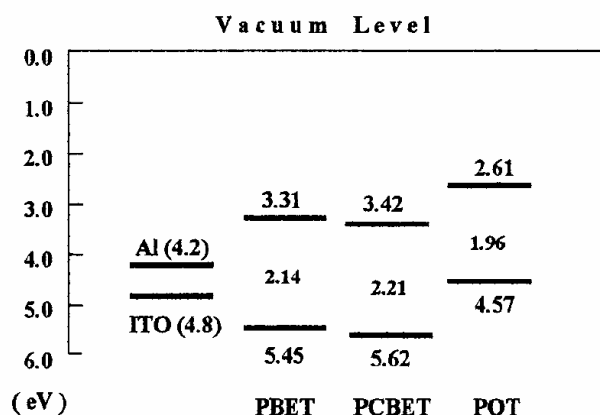


Figure 24. Energy diagram of substituted PT **Comp. 398** (PBET), **Comp. 399** (PCBT) and **Comp. 386** (POT). [From Ref. 471, © 2001 American Chemical Society].

Table 5. Properties of poly(3-R)thiophenes, prepared by the Ulmann, Yamamoto or FeCl_3 polymerization

Polymer (method)	M_n /PDI	$\lambda_{\text{max}}^{\text{abs}} / \text{nm}$ (solution)	$\lambda_{\text{max}}^{\text{abs}} / \text{nm}$ (film)	$\lambda_{\text{max}}^{\text{PL}} / \text{nm}$ (Φ_{fl} / %)	$\lambda_{\text{max}}^{\text{PL}} / \text{nm}$ (film) (Φ_{fl} / %)	$\lambda_{\text{max}}^{\text{EL}} / \text{nm}$ ($\Phi_{\text{EL}}^{\text{ex}}$ / %)	Ref.
Comp. 386						1.8eV	462
Comp. 386 (FeCl_3)	16,800/6.22		500		655	650 (0.012%) ^c	471
Comp. 387 (50% HT)	4,000/1.7	413/ CHCl_3	420	567, 600 (9%)	608 (0.8%)		472
Comp. 387 (60% HT)	3,000/1.6	420/ CHCl_3	432	572, 600 (12%)	608, 643 (0.3%)		472
Comp. 387 (70%-HT)			456		650	630 (1.3×10^{-5} %) ^c	433
Comp. 387 (80% HT)	40,000/2.3	440/ CHCl_3	518	580, 614 (14%)	670, 714 (0.2%)		472
HT-Comp. 387 (98%-HT)			510		717	662 (3.85×10^{-4} %) ^c	433
Comp. 388			496				
Comp. 389 (Ni)	5,900/1.4	451/toluene	550				465
Comp. 390 (Ni)	9,900/1.5	450/toluene	535				465
Comp. 391 (Ni)	9,450/1.6	448/toluene	530				465
Comp. 391 (Ni)	8,000/2		470		660	635	464
Comp. 392 (Cu)	3,030/2.3	423/THF	447	570/THF	620		468
Comp. 393 (Cu)	4,060/1.9	430/THF	450	568/THF	630		468
Comp. 392 (Ni)	3,050/3.2	408/THF	429	555/THF	595		468
Comp. 393 (Ni)	3,510/2.8	408/THF	430	555/THF	600		468
Comp. 392	6,700/2.5	410/THF	434		600	600 (0.016 %) ^c	476
Comp. 393	9,400/3.2	439/THF	460		610	615 (0.018 %) ^c	476
HHTT-Comp. 392	8,100/1.8	387/THF	377		590	590 (0.0085%) ^c	476
HHTT-Comp. 393	8,700/2.0	389/THF	381		600	600 (0.0047%) ^c	476
Comp. 395 (FeCl_3)	3,100/2.8		400	525/ CHCl_3		600 ^d	470
Comp. 396 (FeCl_3)	3,400/1.6		440	534/ CHCl_3		607 ^d	470

Comp. 398 (FeCl ₃)	17,000/2.07		444		580	580 (0.09%) ^c	471
Comp. 399 (FeCl ₃)	20,000/1.89		446		588	600 (0.04%) ^c	471

^a 85% head-to-tail; ^c ITO/Polymer/Al; ^d ITO/PEDOT/Polymer/Al; ^e ITO/Polymer/Mg/Al.

3.2.2 The effect of regioregularity of polythiophenes on EL.

The above mentioned aspect of regioregularity in PTs plays an important role in their bandgap control. The random polymerization of 3-alkylthiophenes leads to a large degree of HH-coupling in the polymer (which are the sites, showing the largest twist distortion between the thiophene units) and decreases the effective conjugation length, whereas HT-regioregular PTs show larger conjugation length and red shift of their absorptions and PL.

Xu and Holdcroft studied the effect of regioregularity on luminescent properties of P3HT **Comp. 387**.⁴⁷² They found that increasing the percentage of HT coupling in P3HT from 50%-HT to 80%-HT results in red shifts of both absorption and emission maxima as well as in increased fluorescence efficiency in solution from 9% to 14% (Table 1). On the other hand, an increased planarization of regioregular HT polythiophene facilitates the aggregation, which results in decrease of the Φ_{PL} emission efficiency in the solid state (from 0.8% for 50%-HT to 0.2% for 80%-HT). Later McCullough performed comparative studies on EL performance of HT-regioregular and regiorandom P3HT **Comp. 387**.⁴³³ The HT-regioregular polymer showed a narrower EL spectrum and ca. twice higher external EL efficiency ($1.5 \times 10^{-4}\%$ vs $7 \times 10^{-5}\%$, at 6 mA current), than non-regular P3HT (Table 5), however, very low Q.E. and observed preferential degradation of LED with irregular P3HT might be responsible for the difference.

Regioregular head-to-tail coupled poly(3-decylthiophene) (**HT-Comp. 388**) is an electroluminescent polymer with well-defined vibronic structure of its absorption spectrum (Figure 25a; 0–0 transition at 2.0 eV) and a red emission with good color purity, which, however, shows a rather low quantum efficiency in the solid state ($\Phi_{\text{PL}}^{\text{film}} = 1 \pm 0.1\%$),⁴⁷³ Its isomer, regioregular head-to-head/tail-to-tail coupled polymer **HHTT-Comp. 388**⁴⁷⁴ shows large blue shifts (Figure 25a) in its absorption, PL and EL spectra and emits green light with one order of magnitude higher PL ($\Phi_{\text{PL}}^{\text{film}} = 11 \pm 0.1\%$) and two orders of magnitude higher EL ($\Phi_{\text{EL}}^{\text{int}} = 0.001$ and 0.25–0.30%, respectively), however, with higher turn-on voltage.⁴⁷³ Both, the blue shifts and the increased emission efficiency of HHTT-regioregular polymer were explained by pronounced inter-annular conformational distortion in its head-to-head fragment ($\sim 70^\circ$ in HH and $\sim 0^\circ$ in HT fragments, as suggested by AM1 semiempirical calculations⁴⁷⁵).

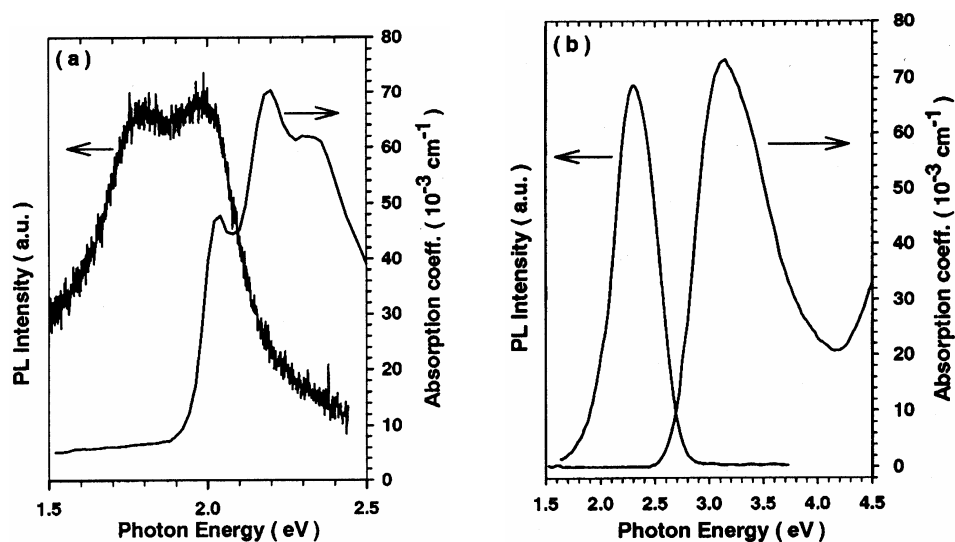
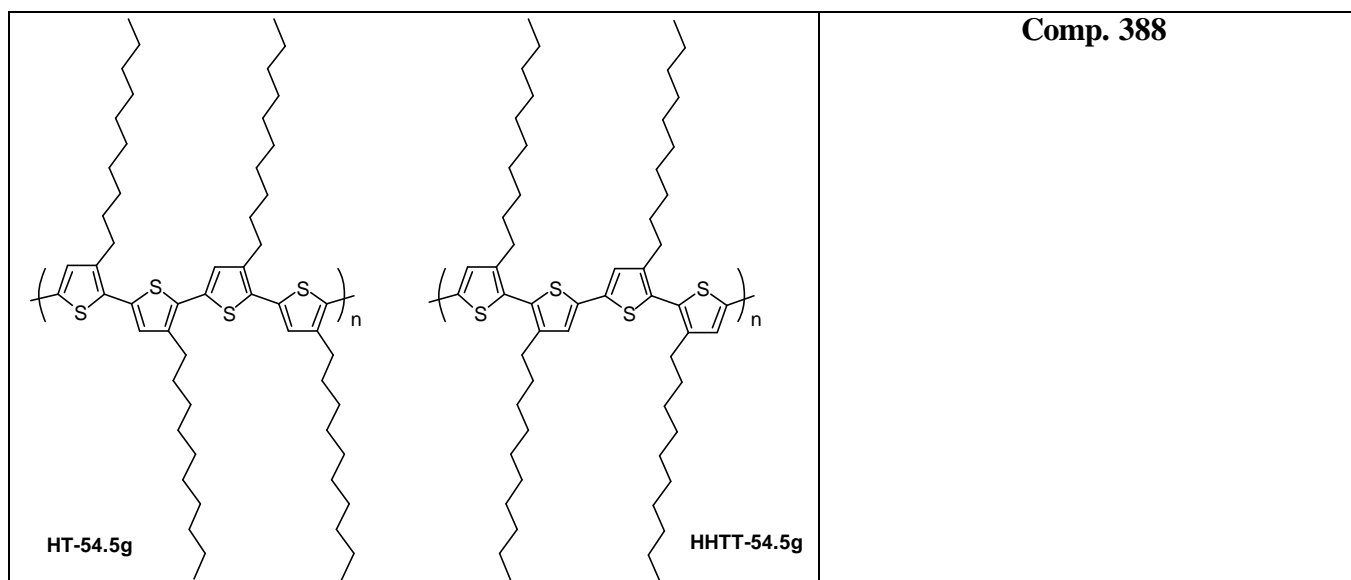
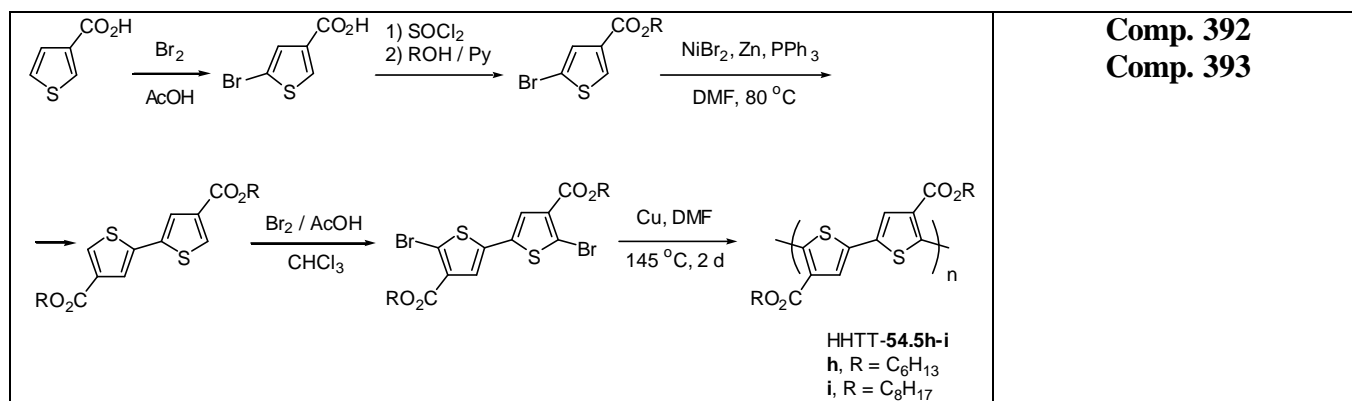


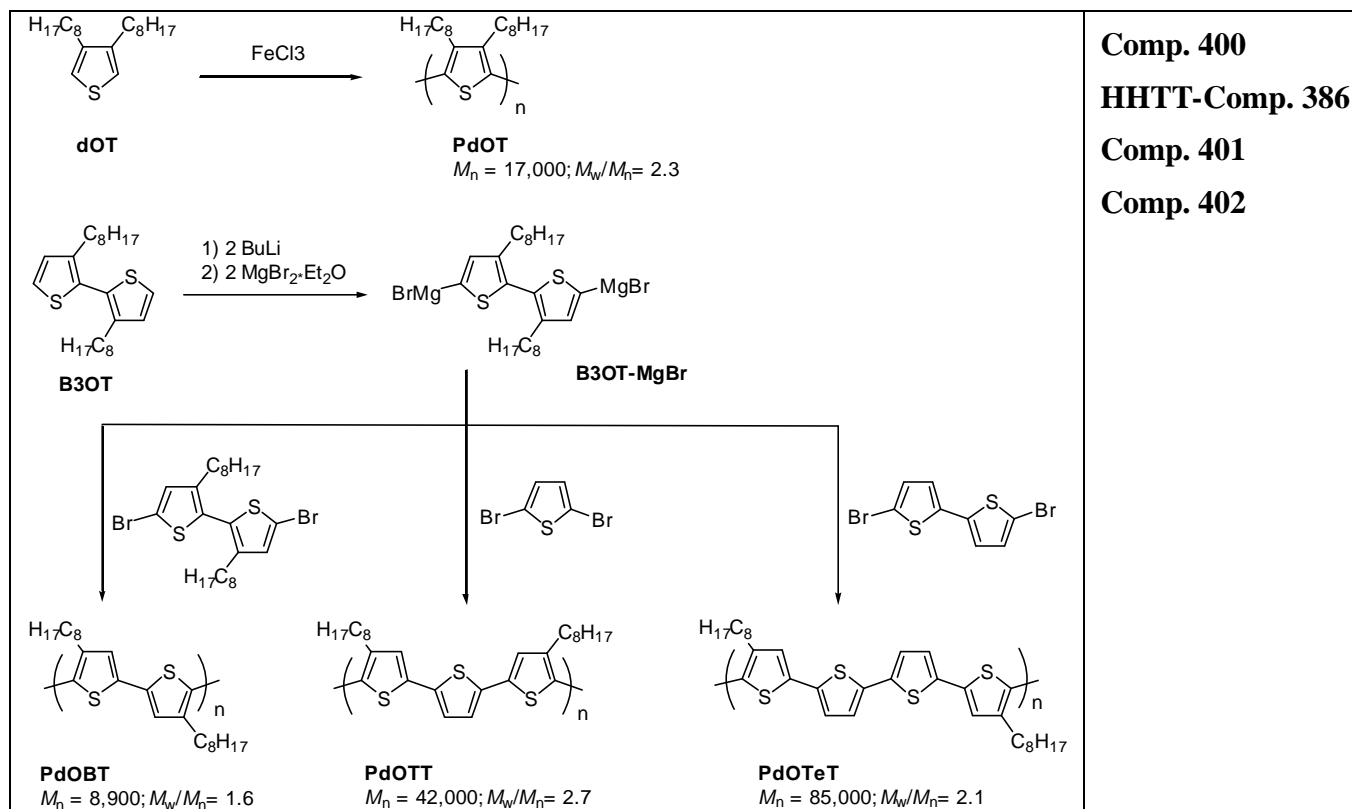
Figure 25. PL and absorption spectra of thin films of regioregular polythiophenes **HT-Comp. 388** (a) and **HHTT-Comp. 388** (b), spin coated on a fused silica substrate. [From Ref. 473, © 1998 American Institute of Physics].

Pomerantz et al. prepared regioregular polymers **HHTT-Comp. 392** and **HHTT-Comp. 393** (Scheme 64) and compared them with previously synthesized⁴⁶⁸ irregular polymers **Comp. 392** and **Comp. 393** (Scheme 61). Regioregular polymers showed blue shifts in absorption for both solution and films (23–30 nm and 57–79 nm, respectively; Table 1), which was interpreted in terms of shorter conjugation length. Blue shifts in PL and EL was much less pronounced (10–15 nm) and PLED showed 2–4 times lower external quantum efficiencies (Table 5).⁴⁷⁶



Scheme 64. Synthesis of regioregular HHTT alkoxy carbonyl-PTs.

Hadziioannou and co-workers synthesized a number of regioregular alkylated polymers **HHTT-Comp. 386**, **Comp. 400–Comp. 402** (Scheme 65) and demonstrated PL and EL color tuning through a variation of the length of the coplanar blocks between the head-to-head links.⁴⁷⁷ They have found blue shifts of more than 100 nm in absorption, PL and EL spectra in the range **Comp. 402** \rightarrow **Comp. 401** \rightarrow **HHTT-Comp. 386** \rightarrow **Comp. 400**, i.e. with increasing the steric hindrance in the polymer backbone. The energies of absorption and emission (PL and EL) maxima were linear functions of the inverse number of thiophene units (1/n) between the two consecutive head-to-head links (Figure 26), which is in agreement with theoretical prediction that the band gap scales linearly with the inverse chain length.⁴⁷⁸ Thus, the results clearly demonstrate that the effective conjugation length is limited by the HH-links in the polymer.



Scheme 65. Synthesis of regioregular HHTT octyl-PTs.

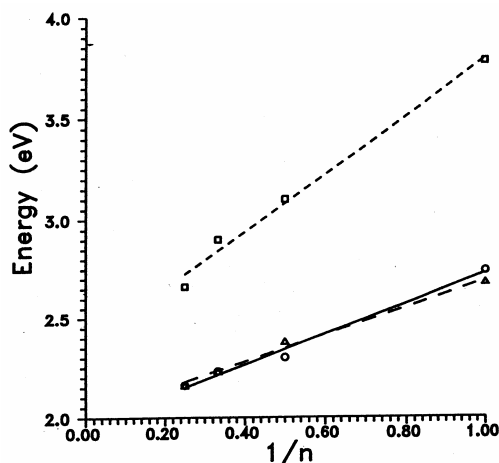


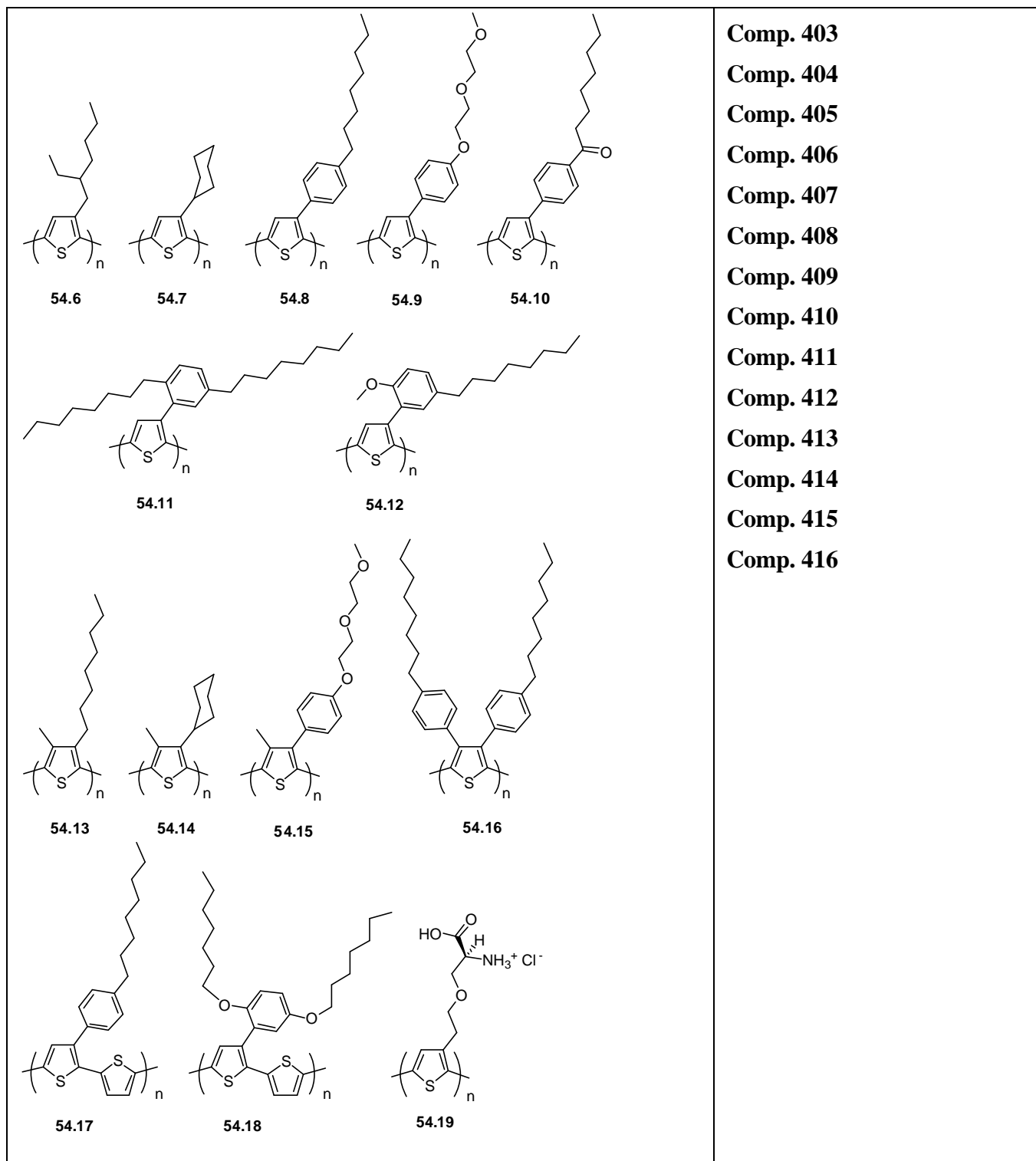
Figure 26. The absorption (□ - - -) and PL (○ - - -) and EL (△ —) energies of polymers **HHTT-Comp. 386**, **Comp. 400–Comp. 402** in thin films vs. an inverse number of thiophene units between the head-to-head links. [From Ref. 477, © 2001 Wiley-VCH].

3.2.3 Emission color tuning in polythiophenes

Although the first publications on EL of poly(3-alkylthiophenes) described materials with red-orange emission (610–640 nm), later a large number of PTs with emissions covering the full visible region, i.e. from blue to red/near-IR, have been reported. These EL color changes can be achieved by structural variations in PT side chains, i.e. by changing the substituents at positions 3 and 4 of the thiophene unit and controlling the regioregularity.

EL color tuning through introduction of various substituents is widely used in other LEPs, where it is also important but, probably, not so impressive. To understand the wide range of colors available from PTs, it is necessary to look on underlying phenomena. The color of the emission of PTs directly depends on the effective conjugation length of the backbone (determined by the twist angle between the thiophene units). The theory predicts a large change in the band gap of polythiophene depending on the torsion angle between consecutive thiophene units: the difference in the band gap of fully planar and 90 ° twisted PTs is as high as 1.7 eV.⁴⁷⁹

These observations inspired Inganäs et al. to exploit the principle of steric hindrance to design the PTs materials with emission colors spanning the full visible spectrum.^{480,481,108} A wide range of 3-substituted and 3,4-disubstituted thiophenes have been synthesized and successfully polymerized by FeCl₃ in chloroform affording polymers **Comp. 403–Comp. 416**.^{449,481,482,483,484}



Although the emission of substituted PTs is not very predictable due to interplay of several factors (steric effects, regioregularity, electronic effects), the full visible range of PL and EL emissions, from red to blue, can be covered by variations of the PT structure via substituents in 3 (3,4) positions (Figure 27). The shift of a band gap can also be seen through the change of electrochemical oxidation potentials of the polymers. Additional evidence for the modification of the effective conjugation in these PTs was also found from Raman spectroscopy studies (shift of the symmetrical C=C stretching:

from 1442 to 1506 cm^{-1}).⁴⁸¹ However, calculating the chromatic coordinates for these polymers showed that they cover only part of the chromatic space (Figure 28): no deep green colors are available in this family of PTs because of broad emission spectra. Some absorption and emission data of these polymers are collected in the Table 6. The large steric hindrances in **Comp. 411** allowed shifting the EL down to 460 nm, with a concomitant drop in quantum efficiency.

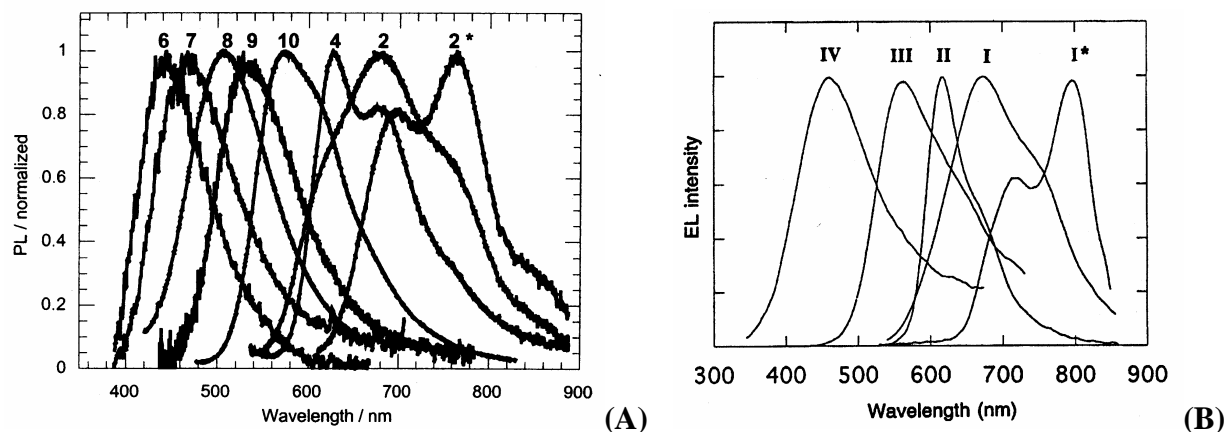


Figure 27. (A) PL spectra from spin-coated films of PTs (2 = **Comp. 405**, 4 = **Comp. 414**, 6 = **Comp. 411**, 7 = **Comp. 410**, 8 = **Comp. 413**, 9 = **Comp. 412**, 10 = **Comp. 404**; 2* = **Comp. 405*** - the film 2 = **Comp. 405** treated with chloroform vapor at room temperature) (from ref. 108) and (B) EL spectra of ITO/Polymer/Ca/Al devices (I = **Comp. 405**, II = **Comp. 414**, III = **Comp. 404**, IV = **Comp. 410**; I* the same as I, upon thermal treatment or by chloroform vapor). [From Ref. 481, © 1995 American Chemical Society].

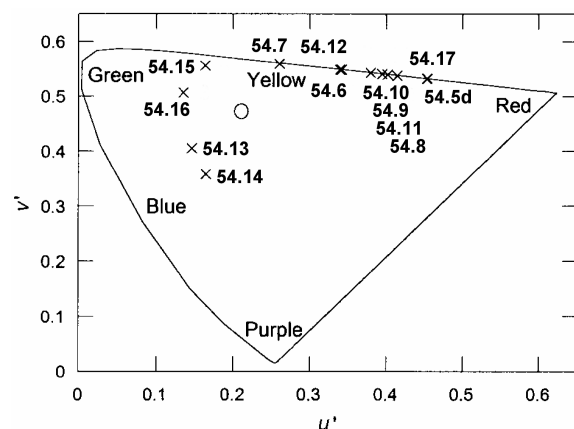


Figure 28. Chromatic coordinates for the polymers **Comp. 386**, **Comp. 403–Comp. 414** and the white spot (?). [From Ref. 108, © 1999 The Royal Society of Chemistry]. *{will be renumbered}*

A certain balance should be kept in distortion of the thiophene planarity as the way to prevent the formation of interchain aggregates. Although introducing two substituents in PT in positions 3,4 does allow to shift the emission through whole visible range and to prevent the interchain interactions (resulting in smaller decrease of the quantum yield in the solid state compared to solution), highly crowded disubstituted PTs **Comp. 410–Comp. 413** show very low luminescence efficiency already in solution (Table 2), because of large distortion of thiophene units in the case of bulky substituents.^{108,481}

In this context, polymer **Comp. 408** represents a well-balanced material showing high PL efficiency in both solution and solid state. The steric factor of dialkylphenyl substituent is similar to those in **Comp. 405–Comp. 407**, as follows from the similarity of their absorption and emission energies. Molecular structure simulation shows that two octyloxy groups in the phenyl ring force its rotation to *ca.* 90 ° out of the thiophene plain. In such configuration, the bulky side chains prevent interchain interaction between the backbones of the polymer molecules, yet allowing the conjugation within the backbone. Spin-coated films of **Comp. 408** show clear vibronic features in both absorption ($\lambda_{\text{max}} = 532 \text{ nm}$, $\Delta E = 0.18 \text{ eV}$) and photoluminescence ($\lambda_{\text{max}} = 659 \text{ nm}$, $\Delta E = 0.16 \text{ eV}$), which, together with very small Stokes shift of only 0.10 eV suggest highly ordered film (Table 6). PLEDs prepared with this polymer in ITO/**Comp. 408**/Ca/Al and ITO/**Comp. 408**/PBD/Ca/Al configurations showed an external efficiencies of 0.1 % and 0.7 %, respectively.⁴⁸⁵

Highly regioregular polymer **Comp. 405** obtained by oxidative polymerization with FeCl_3 (94±2% HT) requires some special attention because it exists in two different forms. In its pristine form, the absorption maximum of spin-coated film is at 493 nm (2.68 eV).^{449,486} On treating the film with chloroform vapors, the maximum is shifted to 602 nm (2.06 eV) and the spectrum shows fine vibronic structure with $\Delta E = 0.19 \text{ eV}$ indicating a more planar ordered conformation (Figure 29A). This conversion can also be achieved by heating the film, and, in contrast to the widely observed thermochromism in polythiophenes, is irreversible, indicating formation of a thermodynamically stable form. The PLEDs prepared with spin-coated **Comp. 405** show red EL centered at 670 nm (1.85 eV). When the diode is heated, the emission is shifted continuously well into the near infrared with heating time and with an increase in temperature. On prolonged heating **Comp. 405** is converted into an ordered film with an EL emission maximum at 800 nm (1.55 eV) (Figure 29B).⁴⁸⁷ It is noteworthy that simple treating with chloroform vapor, although the mechanism of its action is not understood, results in a more pronounced ordering of the polymer, than heating at 200 °C.

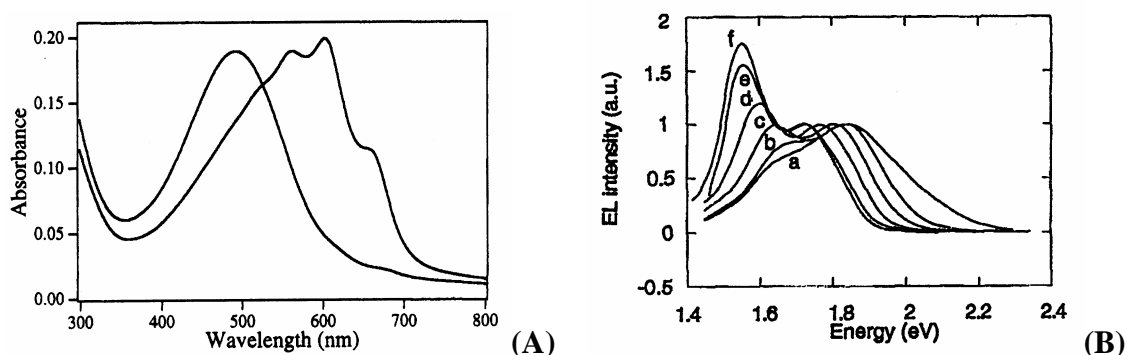
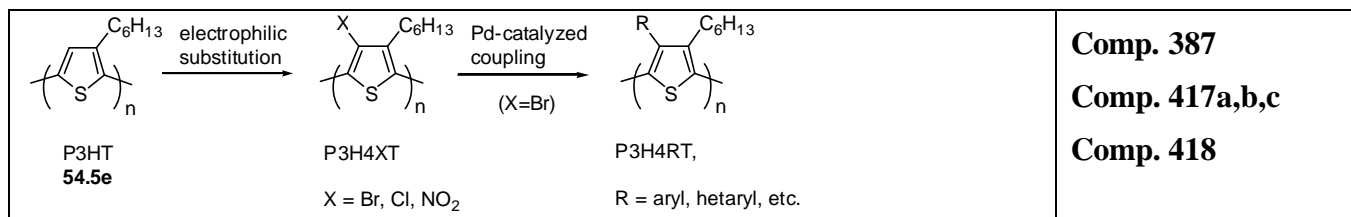


Figure 29. (A) UV-Vis absorption spectra of a spin-coated film of **Comp. 405** on glass ($\lambda_{\text{max}} = 493 \text{ nm}$) and the same film treated with chloroform vapor ($\lambda_{\text{max}} = 602 \text{ nm}$, $\Delta E = 0.19, 0.15, 0.19 \text{ eV}$) [ref. 449, © 1994 Amer. Chem. Soc.] and (B) EL of ITO/**Comp. 405**/Ca/Al device at different heating temperatures: (a) unheated device; (b) $T = 100 \text{ }^{\circ}\text{C}$, 6 s; (c) $100 \text{ }^{\circ}\text{C}$, +6 s; (d) $200 \text{ }^{\circ}\text{C}$, +10 s; (e) $200 \text{ }^{\circ}\text{C}$, +20 s; (f) treated with chloroform before evaporating the contact. [From Ref. 487, © 2001 American Institute of Physics].

As an alternative strategy, the high luminescence efficiency observed in solution can be preserved by diluting the polymer in inert solid matrix. A possible problem of phase segregation can be solved by careful design of the polymer and the matrix. Thus, the polymer **Comp. 416**, when blended with polyacrylic acid (PAA) matrix, did not suffer from phase segregation due to attractive ionic/hydrogen bonding interactions between the PT and the matrix.^{485,488} As a result, the PL quantum

efficiency of **Comp. 416**:PAA (1:100) was 16 % (*cf.* 26% in solution), which is much higher than in **Comp. 416** film (4%). Unfortunately, no PLED with the material was reported, and one can suggest that the performance of such device would be extremely low due to very low concentration of the emitting (and conducting) component.

Another approach to tuning the optical properties and improving the emission of PT derivatives in the solid state was proposed by Holdcroft and co-workers.⁴⁸⁹ They used post-functionalization of P3HT **Comp. 387** by electrophilic substitution reaction (to afford polymers **Comp. 417**) or by Pd-catalyzed coupling (Suzuki, Stille or Heck methodologies) of **Comp. 417a** (to afford polymers **Comp. 418**).⁴⁹⁰ In this case, functionalization with bulky aryl substituents (**Comp. 418**) allowed substantial increase of Φ_{PL} in the films from 1.6 % to 13–22 %.



Saxena and Shirokdar prepared co-polymers **Comp. 419** by oxidative (with FeCl₃) polymerization of a mixture of 3-hexyl and 3-cyclohexylthiophenes, varying the ratio of monomers from 1:9 to 9:1. The co-polymers emitted yellow-green to green light (550–580 nm) and the ITO/**Comp. 419**/Al devices showed external Q.E.s in the range of 0.002–0.016 %.⁴⁹¹ However, even for the best emissive co-polymer (x:y =2:3) the external Q.E. was only 0.016% (and the charge carrier mobility was found to be $5.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).

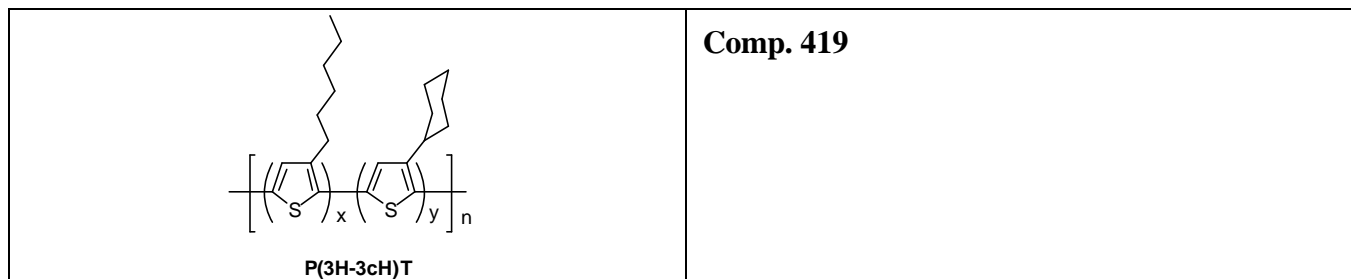


Table 6. Tuning the properties of electroluminescent PTs via conjugation control.

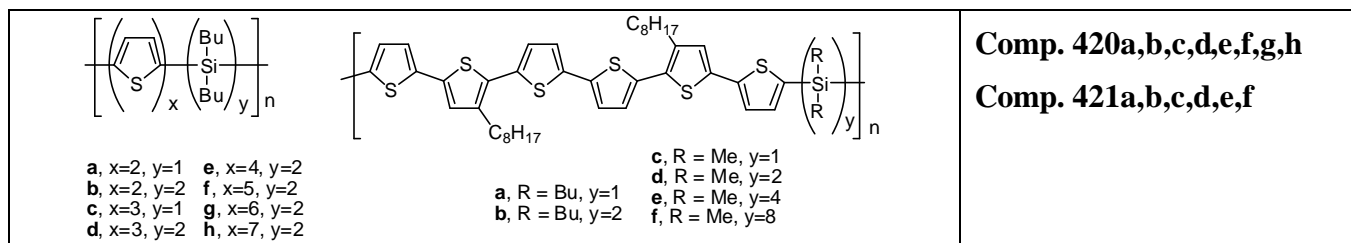
Polymer (regioregularity, %HT)	M_n , g/mol	λ_{abs} , nm (film)	λ_{PL} , nm (film)	Φ_{PL} , % (CHCl ₃)	Φ_{PL} , % (film)	λ_{EL} , ^b nm	Φ_{EL} , ^{ex b} %	Turn-on voltage, V	Ref.
P3OT Comp. 386 (70)	35,000/3.14	506		27	4				108
Comp. 403 (~70)		464	593	26	9				108
Comp. 404 (77)	6,000/9.3	405 [413 ⁴⁸¹]]	574	27	9	555	0.01 (7V)	2.4	108,4 81
Comp. 405 (94)	8,000/6.25	482 (555 ^a)	677 (764 ^a)	18	9 (3 ^a)				108

	23,000/2.26	485	670			670	0.3 (6V)	1.4	481
Comp. 406 (88)	7,800/3.2	476 (552 ^a)	616 (783 ^a)	20	8				108
Comp. 407 (85)	9,400/2.9	454 (555 ^a)	638 (795 ^a)	14	10				108
Comp. 408 (90)	36,000/1.94	494, 532, 577	606, 659, 720	37	24		0.1 ^b / 0.7 ^c		108,4 85
Comp. 409 (90)	46,000/3.48	470	590	29	11				108
Comp. 410	42,000/2.17	326	468	4.6	2.2				108
Comp. 411	26,000/2.77	303 [305 ⁴⁸¹]	442	1.3	0.8	460 ^c	0.6(25V) ^c <0.0001 (4V)	7 ^c	108,4 81
Comp. 412	16,000/3.0	380	532	3.8	2.8				108
Comp. 413	21,000/3.0	346	504	1.1	1.0				108
Comp. 414	9,000/9.1	513 [518 ⁴⁸¹]	627	27	5	610	0.1 (8V)	1.6	108,4 81
Comp. 415	24,500/4.3	510	598	31	4				108
Comp. 419			550–580				0.002–0.016 (2.8–3.6V)		491
Comp. 420a	2,300/2.0	332	428						492
Comp. 420b	3,400/3.4	342	429,470,520			415,474, 508			492
Comp. 420c	5,000/5.0	384	524						492
Comp. 420d	6,800/6.8	389	470,525						492
Comp. 421a	4,300/4.3	443	605			607			492
Comp. 421b	5,600/5.6	451	620			612			492

^a Annealed film; ^b ITO/Polymer/Ca/Al; ^c ITO/Polymer/PBD/Ca/Al.

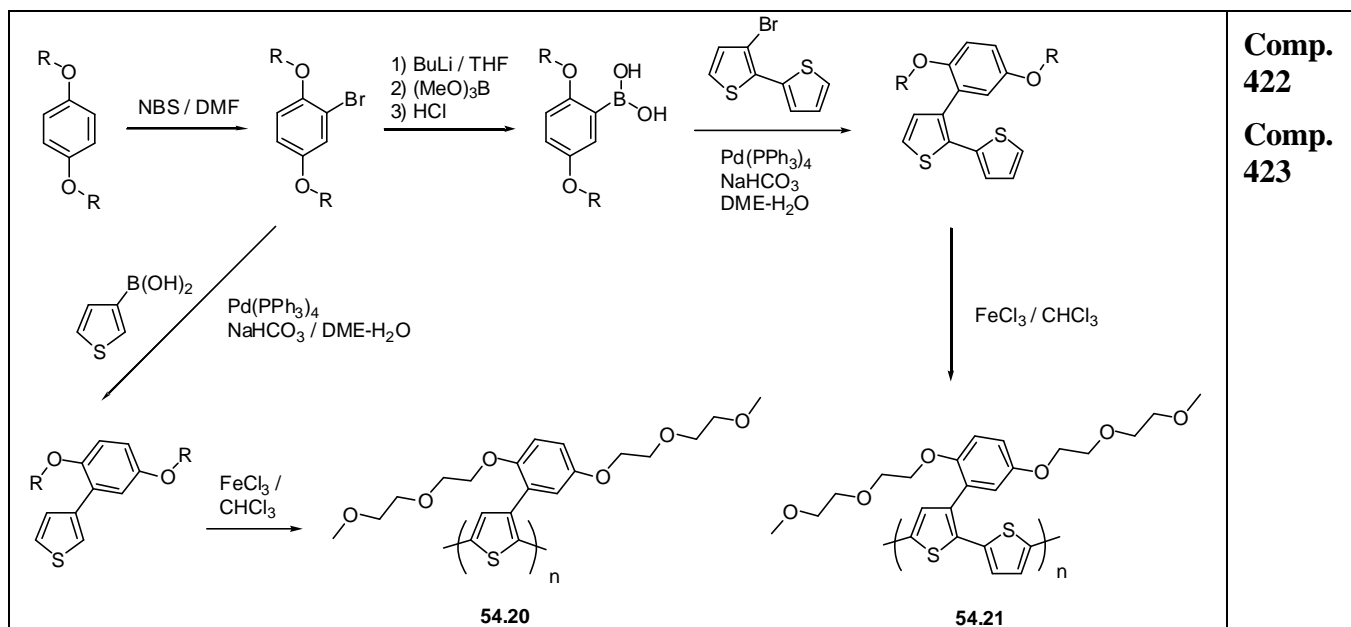
3.3. Light-emitting thiophene block co-polymers with conjugation break.

The above approaches used the idea of conjugation length control in PTs by distorting the polymer backbone via introducing bulky substituents as side groups. Hadziioannou and co-workers demonstrated PL and EL tuning via exciton confinement by design of block co-polymers **Comp. 420a-d** and **Comp. 421a-f** containing oligothiophene and alkylsilanylene units.^{492,493} Precise control of the conjugation length of the oligothiophene blocks interrupted by silanylene units allowed to tune the emission from blue to orange-red (Table 6). Later, Yoshino et al. reported similar extended block-co-polymers **Comp. 420d-h**, which showed changes in color of EL from green to red with increasing length of oligothiophene blocks.⁴⁹⁴



3.4. PTs for light-emitting electrochemical cells.

Two polymers with hydrophilic oligo(ethylene oxide) side chains, **Comp. 422** and **Comp. 423**, have been synthesized (Scheme 66) and studied in light-emitting electrochemical cells (LECs).⁴⁹⁵ Under applied bias, p-doping of the EL polymer took place at the anode whereas at the opposite electrode the cathode material was reduced, although the achieved external Q.E. was relatively low ($\sim 10^{-2}$ %).



Scheme 66. Synthesis of oligo(ethylene oxide)-contained PTs.

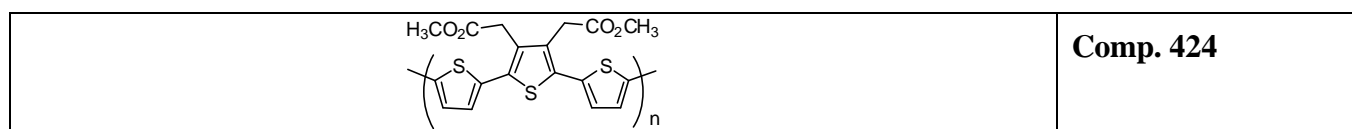
3.5. Blends of polythiophenes.

It was demonstrated that the blends of 3-(3,4-) substituted PT derivatives of different band gaps allow to construct a voltage controlled variable color light source.⁴⁹⁶ Because of different turn-on voltages of high- and low-bandgap polymers, the emission color can be potentially tuned applying different bias: when a relatively low voltage was applied to the polymer blend PLED, the low-bandgap polymer started to emit first, followed by high band-gap emitters when the voltage increased. An effective phase separation, however, is required to minimize the Förster energy transfer onto the low-band gap species. The blend of PTs **Comp. 411:Comp. 414** (50:50%) at 22 V showed EL at ca. 630 nm originating from the emission of **Comp. 414**. When the voltage was increased an additional

emission at ca. 440 nm (corresponding to the EL of **Comp. 411**) appeared, reaching a comparable intensity at 27 V.^{496,497}

Another combinations of PTs in a blend, **Comp. 410:Comp. 404: Comp. 414:PMMA** (10:4:1:1) allowed EL emission of the ITO/Polymer blend/PBD/Ca/Al device at 20 V to be very close to the equi-energy white point as defined by the CIE, while providing relatively high external Q.E. of 0.4–0.6% (at 20 V) (Figure 30).⁴⁹⁸ PMMA was used in this case to diminish the energy transfer from the high-bandgap to the low-bandgap polymers, and several other inert polymer matrixes [polystyrene, polycarbonate, polyvinylchloride, poly(2,6-dimethyl-1,4-phenyleneoxide)] showed similar effects.⁴⁹⁹

Destri et al. reported on electrochemical synthesis of polymer **Comp. 424**, which presented a mixture of oligomers up to dodecamer. According to a MALDI-TOF mass-spectrum a maximum peak corresponded to the tetramer (12 thiophene units). Whereas the ITO/**Comp. 424**/Ca/Al device emits red light (580–650 nm), comparable to that for regioregular PATs, blending **Comp. 424** with PVK and PBD resulted in white emitting diode with 0.03% EL efficiency.⁵⁰⁰ Blending with PBD also was effective to increase the external Q.E. of highly sterically hindered disubstituted PT **Comp. 411** from <0.0001 % to 0.6 % with no change in EL maximum.⁴⁸¹



The emission spectrum of some PT/PBD polymer bilayer devices cannot be explained by a linear combination of emissions of the components. Thus, white emission of the PLEDs ITO/**Comp. 414**/PBD/Al, which showed $\Phi_{\text{EL}}^{\text{ext}}$ of 0.3 % at 7V, consisted of blue (410 nm), green (530 nm) and red-orange (620 nm) bands. Whereas the first and the last EL peaks are due to the EL from the PBD and the PT layers, respectively, the green emission probably originates from a transition between electron states in the PBD layer and hole states in the polymer layer.⁵⁰¹ Similar results (additional green-blue EL at ~495 nm) were demonstrated by PLED ITO/**Comp. 414**/PBD/Ca/Al.⁵⁰²

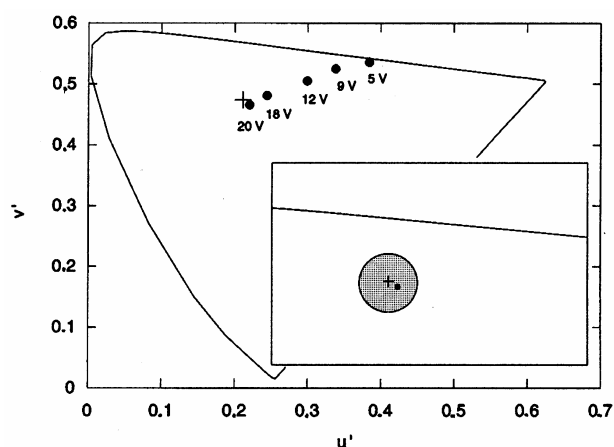


Figure 30. Chromaticity diagram showing the color of the LED with **Comp. 410:Comp. 404:Comp. 414:PMMA** (10:4:1:1) polymer blend at different voltages. Inset: magnified part of the chromaticity diagram; the shaded circle represents the area, which is defined as white (radius 0.028 and centered at equi-energy white point; the $u'-v'$ coordinates are 1976 modification of CIE xy coordinates, the white point $x=y=0.33$ corresponds to $u'=0.211$, $v'=0.474$). [From Ref. 498, © 1996 American Institute of Physics].

Blending low bandgap PTs with other electroluminescent polymers was used to increase the EL efficiency of PLED and it was demonstrated that only small additions of PTs can improve the device performance. The external Q.E. of red-emitting ITO/P3HT(**Comp. 387**):MEH-PPV/Ca diodes initially increased with P3HT content and went through a maximum at 1 wt.% of P3HT with $\Phi_{\text{EL}} = 1.7\%$,⁵⁰³ which is 2–3 times higher than in neat ITO/MEH-PPV/Ca diode and three orders of magnitude higher than in ITO/P3HT(**Comp. 387**)/Ca diode. Later, List et al. reported similar observation of efficient yellow light emission from the blend of blue-emitting ladder poly(*p*-phenylene) (LPPP **Comp. 524b**, see below) with small additions (0.5–2 %) of orange emitting **Comp. 388**.^{504,505} When the concentration of P3DT **Comp. 388** was as small as 1 %, the external EL efficiency of the Al/Polymer blend/ITO device was also significantly higher (4.2 %) than in pure LPPP **Comp. 524b** (2 %).

3.6. Polythiophenes for structured/polarized PLEDs.

Apart from the tunable color emission covering full visible range, white emission from precisely prepared blends of PTs with different band gaps, and internal color conversion of other LEP by adding small amounts of PTs, there are several other aspects explaining the interest in polythiophenes for PLEDs. PTs as classical conjugated polymer with intrinsic one-dimensionality of the polymer chain, could show an anisotropy of their macroscopic properties such as electrical transport or optical properties, when the polymer is aligned. Polarized EL with external Q.E. of 0.05 % was observed in multilayer LB-film PLED ITO/**Comp. 391**/Al, with the ratio in EL between the parallel and perpendicular orientations of 1.3.⁵⁰⁶ Even higher ratio of 2.4 was achieved in ITO/**Comp. 414**/Ca/Al diode made from a stretch-oriented polymer film.⁵⁰⁷

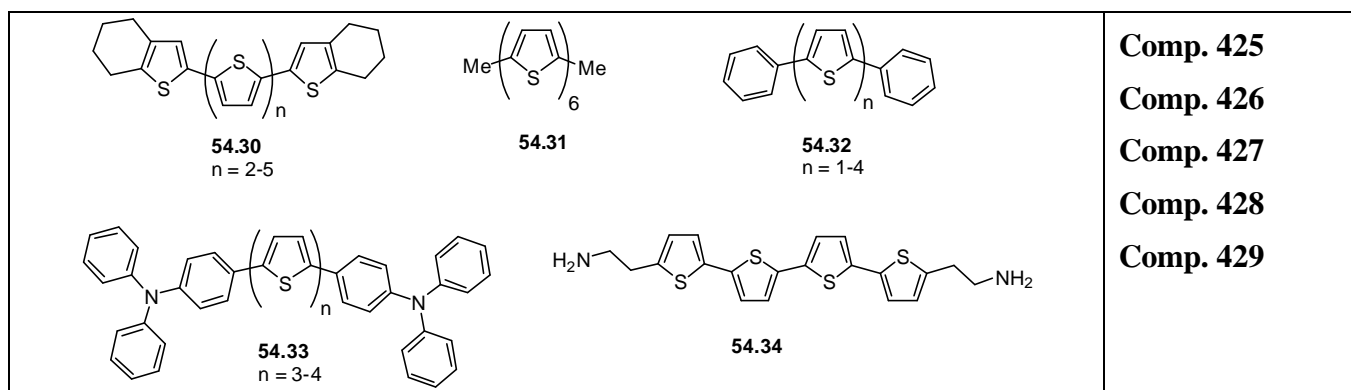
Among other specific applications of PTs as light-emitting materials, it is necessary to mention microcavity LEDs prepared with PTs **Comp. 414** and **Comp. 408**^{508,509} and nano-LEDs demonstrated for a device with patterned contact structure and PT **Comp. 414** blended in PMMA matrix, which emits from the phase separated domains with sizes of 50–200 nm.^{510,511}

3.7. Electroluminescent Oligothiophenes.

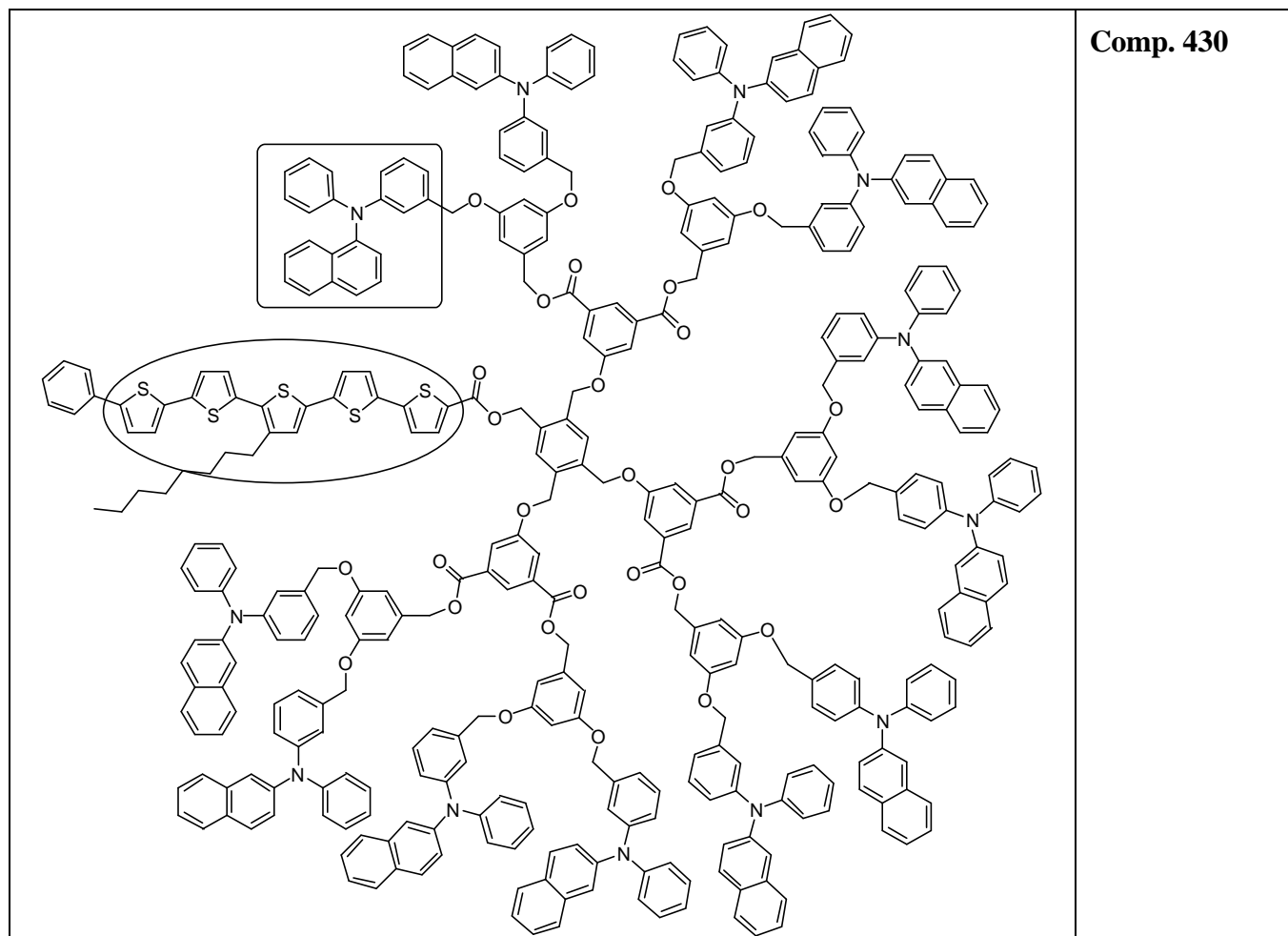
High order and crystallinity of oligothiophenes observed in the solid state determine their unique optical and electrical properties: high charge carrier mobility, anisotropy of electrical and optical properties, etc. Particularly, oligothiophenes are widely studied in FET showing high level of hole and electron mobilities and high on/off ratio. In this context one would expect poor suitability of such materials as light emitting layers in LED. Nevertheless, several publications demonstrate electroluminescence from the oligothiophene-based LEDs. For deeper understanding the effect of effective chain length on the electrical properties and emission in PTs Geiger et al. studied a series of end-capped oligothiophenes **Comp. 425**.⁵¹² The ITO/**Comp. 425**/Al devices prepared by vacuum sublimations of oligomers showed relatively low turn-on voltages of *ca.* 2.5 V and moderate current densities (e.g., 7 mA cm⁻²) with maximum efficiency at *ca.* 8 V, however the EL efficiency was quite low (estimated internal efficiency $\Phi_{\text{EL}}^{\text{int}} \approx 10^{-2} - 10^{-3} \%$). LEDs showed a red shift in the EL peak with increasing number of thiophene units ($n = 3 \rightarrow n = 5$) and a linear dependence of the EL band energy on the inverse number of monomer units. Averaging over EL, PL and absorbance data, the effective conjugation length was estimated at approx. 9–10 thiophene units.

Several other oligothiophenes were studied in this aspect. Variations in the main chain length of phenyl end-capped oligothiophenes **Comp. 427** also showed red shifts of absorbance (from 375 to 524 nm) and emission (from 470 to 620 nm) with increasing number of thiophene units.^{513,514,515}

Sexithiophene end-capped with CH_3 groups (**Comp. 426**) in ITO/**Comp. 426**/Al configuration (vacuum-sublimed) showed red-orange emission with very low Q.E. of $\sim 10^{-9} \%$.⁵¹⁶ Low efficiencies of LEDs, based on crystalline oligothiophenes were somewhat improved by end-capping of terthiophene and quaterthiophene with triphenylamino groups (**Comp. 428**) which led to stable amorphous glasses with luminescence efficiencies of 0.03 and 1.1 lm/W, respectively (at a luminance of 300 cd/m^2).^{517,518} A double-layer device with oligomer **Comp. 428** ($n=3$) as emitting layer and Alq3 as electron-transporting layer showed significantly improved performance, exhibiting a maximum luminance of $13,000 \text{ cd/m}^2$ at driving voltage of 18 V. Undoubtedly, improving the hole transport properties in these oligomers by end-capping with triphenylamino fragments is also an important factor. Terthiophene end-capped with 2-aminoethyl groups was also used in hybrid organic-inorganic perovskite materials. When **Comp. 429** was incorporated within lead halide perovskite layers in ITO/**Comp. 429**: PbCl_4 /OXD7/Mg/Ag device (OXD7 is 1,3-bis[4-(*tert*-butylphenyl)-1,3,4-oxadiazolyl]phenylene), the bright green emission (530 nm) from the organic layer was found.⁵¹⁹

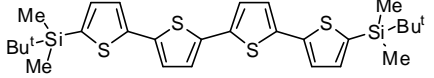
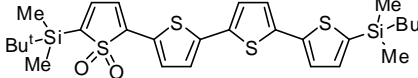
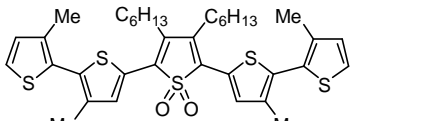
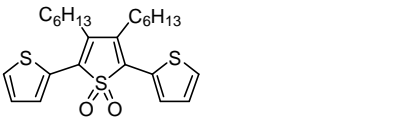


A pentathiophene oligomer unit was used as a core in light-emitting dendrimer with redox-active triarylamino peripherals (**Comp. 430**).⁵²⁰ In this material an excitation of the peripheral amines at 310 nm results in energy transfer to the highly luminescent fluorophore at the core of the dendrimer with subsequent green emission ($\lambda_{\text{PL}} = 550 \text{ nm}$) exclusively from the oligothiophene. In the LED containing also PBD as the electron transporting material, the hole transport occurs solely through peripheral triarylamines whereas the core oligothiophene plays the role of a light emitter. The EL spectrum was essentially identical to PL ($\lambda_{\text{EL}} = 560 \text{ nm}$) with no emission from either PBD (390 nm) or peripheral amines (425 nm) and the maximum external Q.E. was 0.12 %.



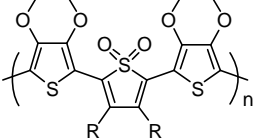
3.8. Thiophene-*S,S*-dioxides as emissive and electron transport moieties.

Poly- / oligo- thiophenes are generally p-type (hole transporting) semiconducting materials. Recently Barbarella et al. reported on novel approach to tailoring the frontier orbitals of thiophene oligomers through a chemical transformation of the thiophene ring into the corresponding thiophene-*S,S*-dioxide (via oxidation with 3-chloroperbenzoic acid).^{521,522} This modification results in "de-aromatization" of the thiophene unit and increases the electron-deficiency, thus offering an efficient methodology to increase the electron delocalization and the electron-transport/injection properties of the material. A comparison of two quaterthiophenes **Comp. 431** and **Comp. 432** indicates that a single thiophene-*S,S*-dioxide moiety leads to only slight increase of the oxidation potential (from 0.95 V to 1.04 V vs. Ag/AgCl) whereas the reduction potential is drastically shifted into positive potentials (from -2.12 to -1.28 V) that results in a bandgap contraction by more than 0.7 eV.⁵²¹ Another feature of such modification is a decreased aggregation tendency resulting in decreased exciton migration to the nonradiative centers. Consequently, oligomers incorporating thiophene *S,S*-dioxide units possess good photoluminescence properties in both the solution and the solid state, as well as high (for PTs) EL efficiency. Particularly interesting in this sense are the oligomers with central location of the thiophene-*S,S*-dioxide unit for which the solid state PL quantum yields were reported to be as high as 37 % (**Comp. 433**)⁵²³ and 45 % (**Comp. 434**)⁵²⁴ (and up to 70 % for thiophene *S,S*-dioxide unit incorporated into oligophenylenes⁵²⁵).

		Comp. 431 Comp. 432 Comp. 433 Comp. 434
TTTT		
		

Incorporation of thiophene *S,S*-dioxide units in oligothiophenes allows to vary both absorption and PL energies in a wide range ($\lambda_{\max}^{\text{abs}} \sim 400\text{--}540\text{ nm}$, $\lambda_{\max}^{\text{PL}} \sim 525\text{--}725\text{ nm}$).^{521,525} Polymers obtained by chemical polymerization of oligomers **Comp. 433** and **Comp. 434** with FeCl_3 showed PL in the NIR region (801 and 910 nm, respectively) although the quantum yields were reported for these materials.⁵²⁵ A non-optimized LED with **Comp. 433** as an active layer (ITO/**Comp. 433**/Ca/Al) showed a luminance of $\sim 100\text{ cd/m}^2$ at 7 V and quite low EL efficiency of 0.03 cd/A at $\sim 180\text{ mA/cm}^2$.⁵²⁶ However, further studies showed that these parameters can be sufficiently improved by blending **Comp. 433** with PVK and introduction of a PEDOT layer: the PLED built as ITO/PEDOT/**Comp. 433**:PVK, 85:15/Ca/Al configuration showed maximum luminance of $\sim 200\text{ cd/m}^2$ at 7 V and EL efficiency of $\sim 0.9\text{ cd/A}$ at 3 mA/cm^2 .⁵²³

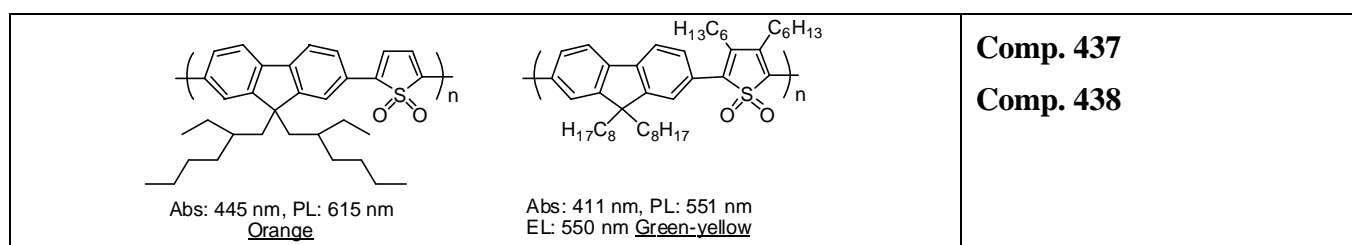
Other thiophene–thiophene-*S,S*-dioxide co-polymers were reported by Berlin et al. who synthesized co-polymers **Comp. 435** and **Comp. 436** with an alternating electronacceptor thiophene-*S,S*-dioxide unit and donor ethylenedioxythiophene (EDOT) units.⁵²⁷ The polymers absorbed at 535 nm ($E_g = 2.3\text{ eV}$) in both the chloroform solution and the films (which is consistent with their electrochemistry: $E_{\text{ox}} \approx 0.40\text{--}0.50\text{ V}$, $E_{\text{red}} \approx -1.75\text{--}1.8\text{ V}$; $\Delta E \approx 2.2\text{--}2.25\text{ V}$) and emitted at 650 nm [$\Phi_{\text{PL}}(\text{film}) \sim 1\%$]. This high band gap [which exceeds that in PEDOT homopolymer by $\sim 0.6\text{ eV}$] strongly suggests a disruption of the conjugation (possibly owing to two alkyl substituents in the thiophenedioxide moiety). The EL emission spectrum was entirely the same as PL emission, and external Q.E. of 0.01 % at 100 cd/m^2 was found for ITO/TPD:**Comp. 435**:PC, (40:40:20)/Ca LED (PC is bisphenol-A-polycarbonate) diode.

 <p style="text-align: center;">R = C₆H₁₃, C₁₂H₂₅</p>	Comp. 435 Comp. 436
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These pioneering works stimulated recent research activities in incorporation of the thiophene-*S,S*-dioxide unit into various co-polymers, and PLEDs built with such co-polymers were reported by several groups. Charas et al. studied PLED based on co-polymer **Comp. 437** (obtained by Suzuki coupling of 2,5-dibromothiophene-*S,S*-dioxide with diboronic ester of 9,9-bis(2-ethylhexyl)fluorene⁵²⁸) and its blends with PFO **Comp. 188**.^{529,530} The co-polymer **Comp. 437** emitted orange light ($\lambda_{\text{PL}}^{\text{film}} = 615\text{ nm}$), and there was a strong suppression of PL quantum yield going from solution to the solid state ($\Phi_{\text{PL}}^{\text{cyclohexane}} = 19\%$, $\Phi_{\text{PL}}^{\text{film}} = 0.5\%$). A single-layer ITO/**Comp. 437**/Ca PLED exhibited quite low EL efficiency ($\Phi_{\text{EL}}^{\text{ex}} = 2.2 \times 10^{-4}\%$), which was attributed to a combination of low PL efficiency and charge transport limitations. Upon inserting a hole-injection PEDOT layer the EL efficiency was increased to $\Phi_{\text{EL}}^{\text{ex}} = 9 \times 10^{-4}\%$ and the maximum luminance increased from 0.2 cd/m^2 to about 5.3

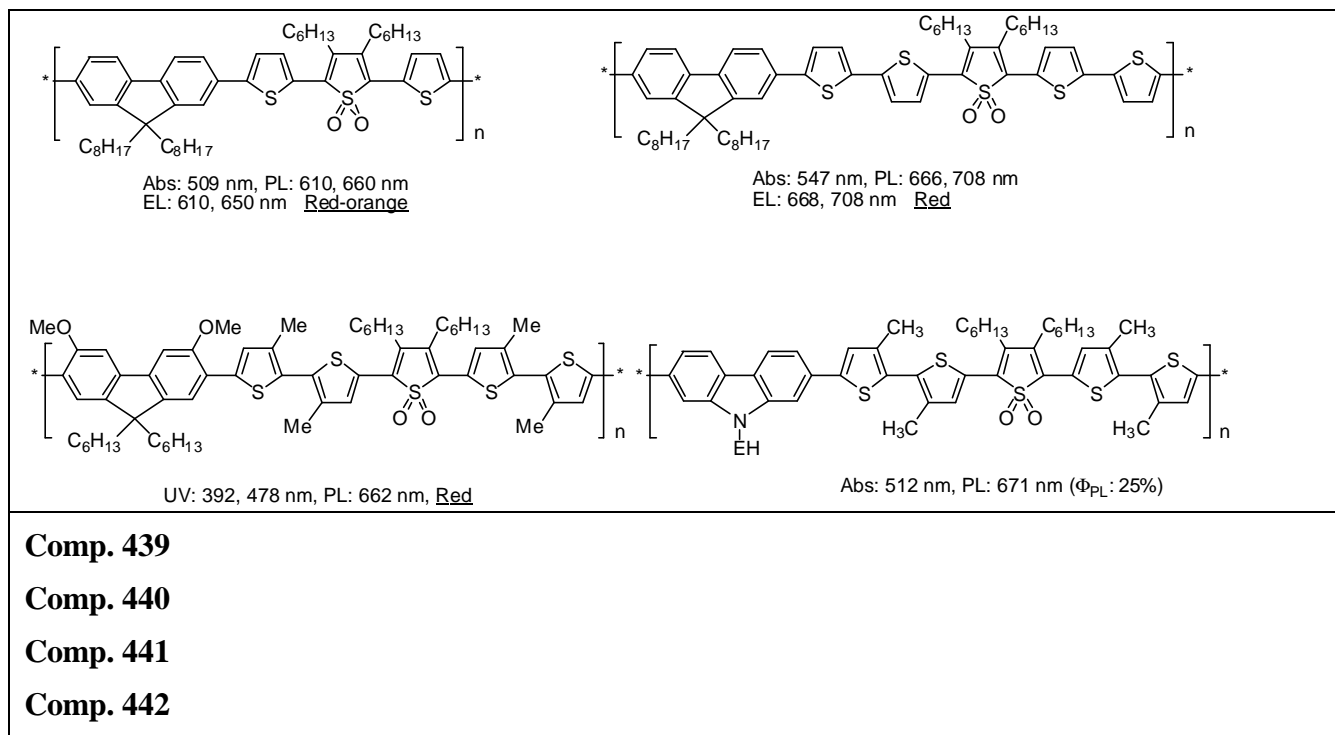
cd/m². The optoelectronic characteristics of the devices were improved by blending **Comp. 437** with PFO, which allowed an increase in external EL efficiency up to 0.21 % (for ITO/PEDOT/PFO:**Comp. 437** (95:5)/PBD/Ca architecture) and a decrease in the turn-on voltage from 16 V to 5–5.5 V. Remarkably, the EL of the blend in this case was almost exclusively from the co-polymer **Comp. 437**, in spite of low ratio of the latter.

The same Suzuki methodology was used in synthesis of similar co-polymer **Comp. 438**.⁵³¹ The polymer showed green-yellow emission, which is solvent-dependent (from 545 nm in THF to 565 nm in chloroform) as often observed for polar chromophores. The PL Q.E. also varied with the solvent (from 11 % in THF to 21 % in decalin), but, in contrast to co-polymer **Comp. 438**, no strong decrease in emission efficiency was observed in the solid state ($\Phi_{\text{PL}}^{\text{film}} = 13\%$), which could be attributed to the effects of substituents at the thiophene ring. LEDs based on **Comp. 438** showed, for ITO/PEDOT/**Comp. 438**/Ca/Al architecture, a turn-on voltage of *ca.* 10 V with a maximal brightness of 340 cd/m² at 22 V and appreciable external Q.E. of 0.14 %.



Beaupré and Leclerc reported fluorene-thiophene co-polymers in which fluorene and thiophene-*S,S*-dioxide fragments were separated by one or two thiophene units (**Comp. 439** and **Comp. 440**, respectively).³⁹¹ The electronic effect of an additional thiophene unit (the system can be viewed as an alternating donor-acceptor polymer) and the planarization factor known for longer oligothiophene units, results in pronounced bandgap contraction. These co-polymers are both p- and n- dopable, as follows from their electrochemistry, with bandgaps of 2.0 and 2.2 eV for **Comp. 439** and **Comp. 440**, respectively. The PLEDs, fabricated in configurations ITO/LiF/Polymer/PBD/LiF/Al/Ag show rather low turn-on voltages of 4 V but the maximal brightness (120 cd/m² at 7V and 15 cd/m² at 8V, for **Comp. 439** and **Comp. 440**, respectively) is lower than that for co-polymer **Comp. 438**. Although highly efficient ($\Phi_{\text{PL}}^{\text{film}} \approx 40\text{--}70\%$) solid state PL was demonstrated from some oligothiophenes and oligophenylenes containing thiophene-*S,S*-dioxide units,⁵²⁵ the efficiency of similar fluorene co-polymers is remarkably lower.

The combination of thiophene and thiophene-*S,S*-dioxide units in a co-polymer allows tuning the emission color from green to pure red.^{532,391} However, the PLEDs fabricated with these materials showed a rather low external Q.E. (< 0.01 %), which further decreases with increasing the number of the thiophene units. Similar results (significant decrease of the PL Q.E.) were observed for thiophene/thiophene-*S,S*-dioxide co-polymers containing 3,6-dimethoxyfluorene (**Comp. 441**²⁹⁹) and carbazole units (**Comp. 442**⁵³³) ($\Phi_{\text{PL}} = 20\text{--}25\%$ in solution).

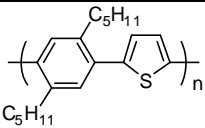
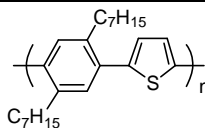


Also, a danger of potential instability towards *n*-doping of the thiophene-*S,S*-dioxide-containing oligomeric and polymeric electroluminescent materials can be foreseen based on the known instability of other classes of heterocyclic systems with SO₂ fragment in the cycle towards reductive cleavage. However, it should be mentioned that such a behavior has not so far been reported for the above thiophene-*S,S*-dioxide-containing materials.

3.9. Co-polymers of thiophenes with other conjugated moieties.

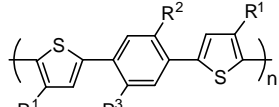
3.9.1. Thiophene co-polymers with aromatic moieties.

Salaneck and co-workers first reported EL from alternating phenylene-thiophene co-polymer **Comp. 444**. Its bandgap, ionization potential and electron affinity, as calculated with the valence effective Hamiltonian (VEH) method, are 3.08, 5.29 and 2.22 eV, respectively.⁵³⁴ These values are between the corresponding values for poly(*p*-phenylene) PPP **Comp. 481** (3.28, 5.43 and 2.15 eV⁵³⁵) and PT **Comp. 377** (1.6, 5.0 and 3.4 eV⁵³⁶). Steric hindrance of side heptyl groups in this polymer results in inter-annular torsion angles of 50°, which is substantially larger than that of PPP (23°); nevertheless its bandgap is smaller than that of PPP. Phenylene-thiophene co-polymers **Comp. 443** and **Comp. 444** emit blue light at ca. 450–475 nm with somewhat different reported external EL efficiencies of ~0.2 %⁵³⁷ and 0.03 %, ⁵³⁸ respectively, both for ITO/polymer/Ca configurations. It has also been shown that the efficiency of the device can be substantially improved (up to 2%) by blending of **Comp. 444** with substituted PPP polymer (**Comp. 484e**, see below) (1:10).⁵³⁷ This is among the highest values reported for thiophene-based LEP.

 <p>Abs: 335 nm, PL: 455 nm EL: 455 nm, $\Phi_{EL}^{ex} = 0.03\%$ <u>Blue</u></p>	 <p>Abs: ~330 nm, PL: ~450 nm EL: ~475 nm, $\Phi_{EL}^{ex} = 0.03\%$ <u>Blue</u></p>	<p>Comp. 443</p> <p>Comp. 444</p>
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An important series of co-polymers **Comp. 445** containing thiophene-phenylene-thiophene repeating units have been reported by Huang et al.^{539,540,541} Polymers were obtained via $FeCl_3$ oxidation of corresponding thiophene-phenylene-thiophene trimers, which were synthesized by Pd-catalyzed coupling of 1,4- R^2 , R^3 -2,5-dibromobenzenes with corresponding 3- R^1 -2-thienylzinc chlorides. Changing the substituents R_1 and R_2 the polymer emission can be tuned from greenish-yellow to pure green. While retaining much of the substituted PT character (e.g., good hole-transport properties and stability), these materials exhibit significantly improved fluorescence efficiency in the solid state (Φ_{PL} up to 29%), which leads to external Q.E. of up to 0.1 % for ITO/**Comp. 445**/Ca PLED (Table 7).

Table 7. Tuning the properties of substituted phenylenethiophene co-polymers.

					Comp. 445					
R^1	R^2	R^3	M_n , g/mol	PDI	λ_{max}^{abs} , nm	λ_{max}^{PL} , nm	Φ_{PL} , %	Φ_{EL}^{ex} , %	Turn-on voltage ^a	Ref
$n-C_6H_{13}$	CH_3	CH_3	20400 12600	2.92 1.48	340 346	477 470	10 15±1	0.004	17	539,541
$n-C_6H_{13}$	H	H	19700 31200	2.74 2.31	396 378	524 505	20 22±2	0.02	13	539,541
$n-C_6H_{13}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$	14600 26100	1.92 1.27	430 405	530 520	29 27±3	0.1	8	539,541
$c-C_6H_{11}$	CH_3	CH_3			360	466	6			539
$c-C_6H_{11}$	H	H			376	495	11			539
$c-C_6H_{11}$	$OC_{10}H_{21}$	$OC_{10}H_{21}$			410	505	16	0.05	9	539
$p-(n-C_4H_9)Ph$	$n-C_{10}H_{21}$	$n-C_{10}H_{21}$	8230	2.19	442	532	11	(~0.1)	(~7)	540
$p-(n-C_4H_9)Ph$	CH_3	2-ethylhexyl	6850	1.51	426	538	12	(~0.1)	(~7)	540
$p-(n-C_4H_9)Ph$	2-ethylhexyl	2-ethylhexyl	4360	1.68	429	533	11	0.1	7	540

^a ITO/Polymer/Ca.

Other widely studied thiophene co-polymers with aromatic units, 9,9-disubstituted fluorenes, have been already described above in the "Polyfluorenes" section.

Alternating oligothiophene-containing co-polymers **Comp. 446–Comp. 450** have 1,1-binaphthyl units, interrupting the conjugation due to large torsion angle between the naphthalene rings. The non-planar structure could prevent the self-quenching processes in the solid state, and variation in the length of the oligothiophene segment from one to seven thiophene rings tunes the emission color from yellow-green to red (Table 8).⁵⁴² A single layer device ITO/**Comp. 447**/Al prepared with co-polymer **Comp. 447** emitted orange light (λ_{EL} at 568 nm with a shoulder at 590 nm) with turn-on voltage of 5.7 V, luminance 25 cd/m² at 8.0 V and external Q.E. of 0.005 %.⁵⁴³

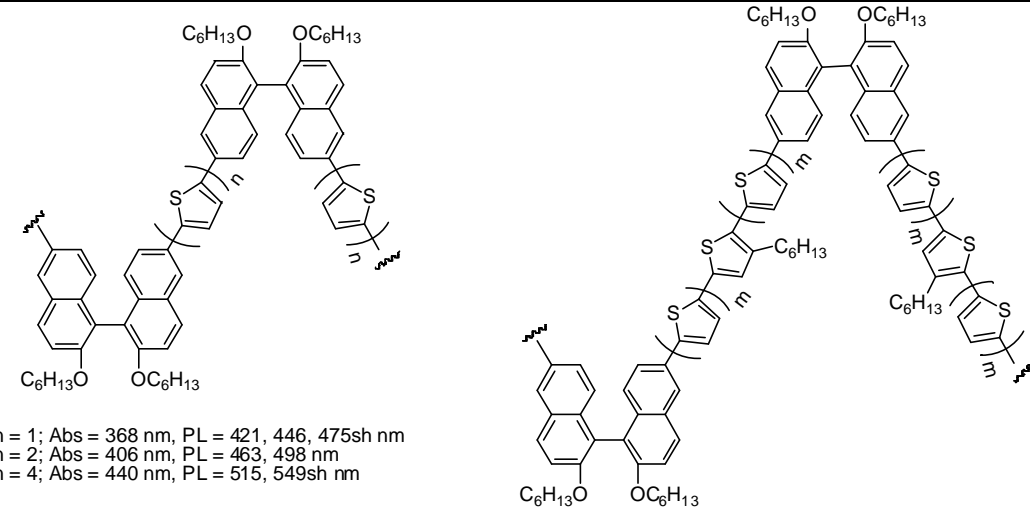
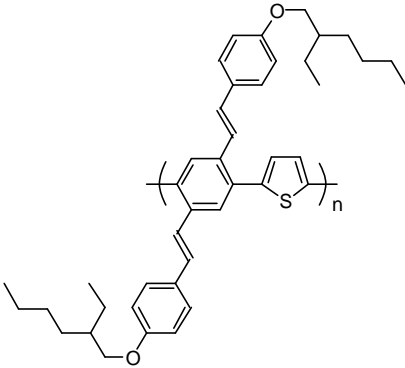
 <p> $n = 1$; Abs = 368 nm, PL = 421, 446, 475sh nm $n = 2$; Abs = 406 nm, PL = 463, 498 nm $n = 4$; Abs = 440 nm, PL = 515, 549sh nm </p> <p> $m = 2$; Abs = 434 nm, PL = 530, 568ch nm $m = 3$; Abs = 454 nm, PL = 545, 583, 631sh nm </p>	<p>Comp. 446</p> <p>Comp. 447</p> <p>Comp. 448</p> <p>Comp. 449</p> <p>Comp. 450</p>
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Table 8. Properties of binaphthyl-linked thiophene block co-polymers with different conjugation length.

Compound	M_n , g/mol	PDI	$\lambda_{\max}^{\text{abs}}$, nm	$\lambda_{\max}^{\text{PL}}$, nm (DCM)	Φ_{PL} , % (DCM) ^a
Comp. 446 , $n=1$	13,900	2.6	368	421, 446, 475sh	54
Comp. 447 , $n=2$	18,100	1.7	406	463, 498	26
Comp. 448 , $n=4$	5,100	1.1	440	515, 549sh	23 (19 ^b)
Comp. 449 , $m=2$	17,400	1.6	434	530, 568sh	5.4 (23 ^b)
Comp. 450 , $m=3$	2,300	2.6	454	545, 583, 631sh	6.5 (7.2 ^b)

^a Excitation at 380nm. ^b Excitation at the longest wavelength absorption maximum.

Co-polymer **Comp. 451** prepared by Stille coupling of dibromophenylene unit with 2,5-bis(tributylstannyl)thiophene, represents another example of phenylene-*alt*-thiophene backbone, where the substituted phenylene unit forms an oligophenylene-vinylene fragment which is not in the main conjugation chain.⁵⁴⁴ A PLED prepared with this polymer (ITO/**Comp. 451**/Al) emitted green light (520 nm) with turn-on voltage of *ca.* 9.5V, but no other data on luminance or efficiency of the device was reported.

 <p>Abs: 362 nm, PL: 530 nm, EL: 520 nm. <u>Green</u></p>	<p>Comp. 451</p>
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3.9.2. Thiophene co-polymers with heteroaromatic moieties.

Several co-polymers (**Comp. 452–Comp. 458**) containing electron-rich thiophene and electron-deficient 1,3,4-oxadiazole units have been reported by Huang and co-workers.^{545,546,547,548} Structural variations, particularly different length of oligothiophene fragments, allowed to tune the bandgap and PL energy of these materials (Table 9). An ITO/**Comp. 452c**/Ca single layer LED emitted blue light with turn-on voltage of 8 V at forward bias. Although the polymer showed very high PL quantum yield of 79 %, the external Q.E. of the device was only ~0.0001 % because of unoptimized device structure and, possibly, a purity problem.

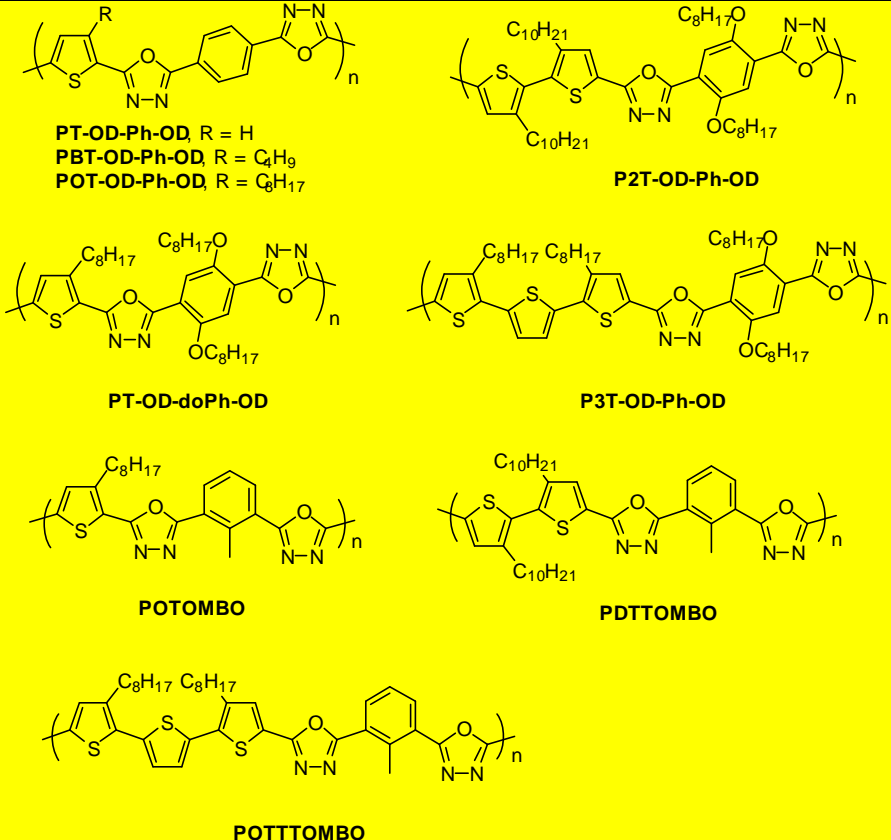
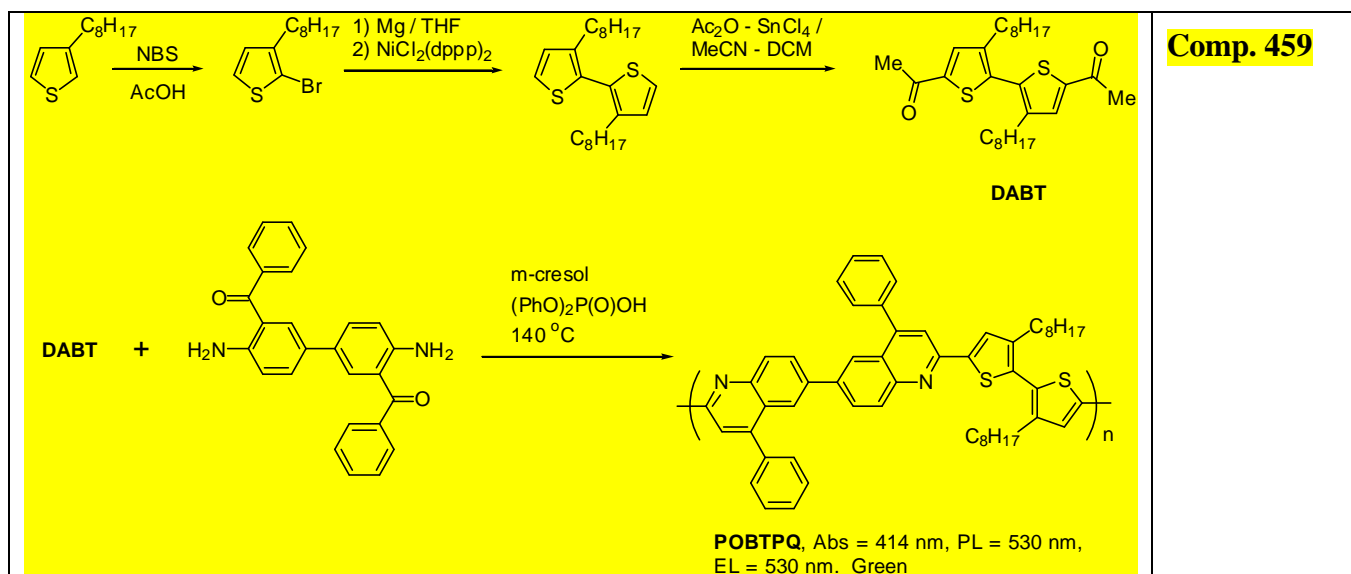
 <p>PT-OD-Ph-OD, R = H PBT-OD-Ph-OD, R = C₆H₉ POT-OD-Ph-OD, R = C₆H₁₇</p> <p>P2T-OD-Ph-OD</p> <p>PT-OD-doPh-OD</p> <p>P3T-OD-Ph-OD</p> <p>POTOMBO</p> <p>PDTTOMBO</p> <p>POTTOMBO</p>	<p>Comp. 452a,b,c</p> <p>Comp. 453</p> <p>Comp. 454</p> <p>Comp. 455</p> <p>Comp. 456</p> <p>Comp. 457</p> <p>Comp. 458</p>
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Table 9. Properties of oxadiazole-thiophene co-polymers.

Compound	M_n , g/mol (PDI)	$\lambda_{\max}^{\text{abs}}$, nm film (solution)	$\lambda_{\max}^{\text{PL}}$, nm film (solution)	Φ_{PL} , %	E_g^{opt} , eV (film)	E_{red} , V
Comp. 452a		(330)	(425)	7.6 ^a	(2.87)	
Comp. 452b		395 (364)	475 (433)	68 ^a	2.83 (2.85)	onset –1.86 (SCE)
Comp. 452c		396, 440sh (375)	486 (438) ⁵⁴⁶ 455, 469, 478 ⁵⁴⁵	79 ^a	2.79 (2.84)	onset –1.88 (SCE) onset –1.54 (Ag/Ag ⁺)
Comp. 454	5419 (1.9)	420, 443	489			pc/pa –1.83/–1.60 (SCE)
Comp. 453	7574 (2.0)	441, 471	530			pc/pa –1.95/–1.70 (SCE)
Comp. 455	2814 (1.4)	439sh, 461, 494sh	580			pc/pa –1.79/–1.70 (SCE)
Comp. 456	3830 (1.8)	358	462		3.04	pc/pa –1.73/–1.53 (SCE); $E_g^{\text{CV}}=3.02$
Comp. 457	24900(1.41)	376 (342 CHCl ₃)	498, 526 (444, 462 CHCl ₃)		2.83	pc/pa –1.86/–1.75 (SCE). $E_g^{\text{CV}}=2.84$
Comp. 458	2870 (2.0)	430	568		2.54	pc/pa –1.76/–1.67 (SCE). $E_g^{\text{CV}}=2.51$

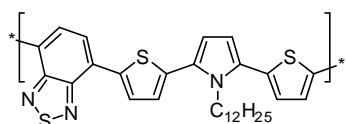
^a Relative quantum yield vs. quinine sulfate.

Jenekhe and co-workers reported the synthesis of another *n*-type conjugated co-polymer with alternating bithiophene and bis-quinoline units, **Comp. 459**, which showed reversible reduction at a formal potential of –1.53 V vs. SCE (onset at ca. –1.4 V) and therefore expected to exhibit good electron transport properties (Scheme 67).⁵⁴⁹ **Comp. 459** emits green light with moderate efficiency in solution (32 %), which, however, dropped down to 4 % in the solid state. The poor luminescence quantum yield of **Comp. 459**, as compared to other polyquinolines, might be due to an intramolecular charge transfer quenching (and, possibly, intermolecular charge transfer for the solid state) in the donor-acceptor co-polymer. As an emissive material, **Comp. 459** exhibits weak green EL (530 nm) with an external Q.E. of 0.05 % for an ITO/PEDOT/**Comp. 459**/Al configuration. However, a large improvement in performance was found for a bilayer device: the PLED ITO/MEH-PPV/**Comp. 459**/Al diode showed bright orange-red EL emission with a turn-on voltage of 8.5 V, a luminance of 2,310 cd/m² at 15 V and a current density of 267 mA/cm²; the external Q.E. of the device, 0.68 %, is more than three times higher than that for MEH-PPV single-layer device (0.02 %). Similarly, this polymer can be used in polymer blend system: a single-layer blend PLED ITO/MEH-PPV:**Comp. 459** (72:28)/Al showed turn-on voltage of 6 V, luminance of 1,480 cd/m² at 14 V and a current density of 279 mA/cm²; the external Q.E. of the device was 0.64 %.



Scheme 67. Synthesis of bisquinoline – thiophene co-polymers. *[do in ChemDraw, not a picture]*

Low band gap ($E_g \sim 1.6$ eV) conjugated thiophene co-polymer **Comp. 460** with pyrrole and 2,1,3-benzothiazole units have been synthesized by Stille coupling.⁵⁵⁰ It showed emission in near IR region ($\lambda_{EL} \sim 800$ nm) with turn-on voltage below 4 V, however with very low efficiency.



Comp. 460

Blending with dialkoxy-PPV **Comp. 14** device (ITO/PEDOT/polymer blend layer/LiF/Ca) substantially improves the EL efficiency (by *ca.* 2 orders of magnitude). A moderately efficient energy transfer from the higher band gap PPV ($\lambda_{EL} = 650$ nm) on PT **Comp. 460** ($\lambda_{EL} = 830$ nm) allows for fine tuning the emission color by changing the components ratio (Figure 31).⁵⁵¹

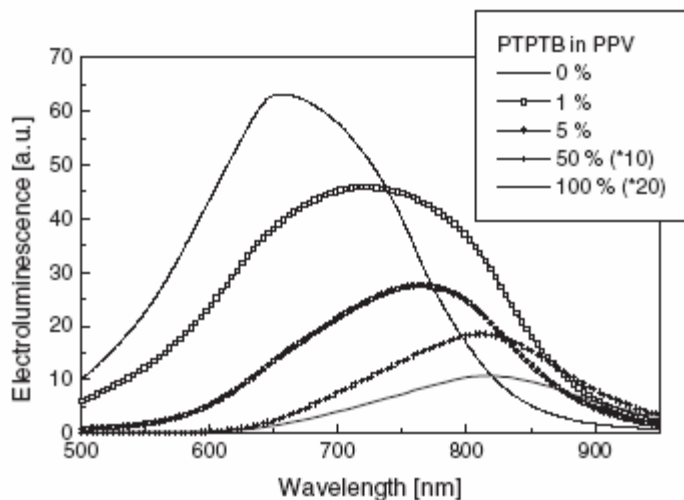
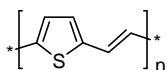


Figure 31. Electroluminescence spectra of ITO/PEDOT/active layer/LiF/Ca devices with **Comp. 460** (PTPTB) and **Comp. 14** (PPV) as an active layer. [From Ref. 551, © 2002 Wiley-VCH].

Oligo-2,5-thienylenevinylenes (OTV) have been recognized as potential class of linear conjugated systems for micro- and nanoelectronics.⁵⁵² Comparison of optical data for OTV with other classes of conjugated oligomers (oligothiophenes, oligo-2,5-thiopheneethynylenes, oligo-1,4-phenylenevinylenes, oligo-1,4-phenyleneethynylenes, oligoacetylenes) shows that OTV exhibit the longest effective conjugation length among the known systems and the smallest $\Delta E_{\text{HOMO-LUMO}}$ values thus promising the lowest band gap for corresponding polymers. We are not aware of any report of poly-2,5-thienylenevinylene (PTV, **Comp. 461**²⁶) being a fluorescent materials, in spite of strong NIR photo- and electroluminescence observed in cyano-substituted PTV (**Comp. 119**⁴⁴). Furthermore, blending 5–25% of PTV **Comp. 461** into PPV **Comp. 1** completely quenches the luminescence of the later, and the resulting blend is not emissive.



Comp. 461

3.10. Conclusions.

Polythiophenes represent an important class of (generally) low band gap conjugated polymers for LED applications, although variation in substituents which change the distortion between the thiophene rings allows tuning the emission in a wide range, from blue-greenish to deep red and NIR. PTs possess a strong aggregation tendency that decreases the PL and EL emission efficiency, but can be minimized by introducing bulky substituents. Regioregularity in mono-3-substituted PTs offers an additional control over the light-emitting properties of these materials. PATs have higher HOMO energies than PPVs or PFs (e.g., for poly-3-octylthiophene: HOMO = -4.57 eV, $E_g = 1.96$ eV) thus decreasing hole injection barrier from ITO electrode.

Relatively efficient blue (polymer **Comp. 411**, external Q.E. = 0.6% ⁴⁸¹), red (polymer **Comp. 408**, external Q.E. = 0.7% ⁴⁸⁵) and white (blend of **Comp. 404**, **Comp. 410** and **Comp. 414**, external Q.E. = 0.3% ⁴⁹⁸) emitters have been reported for thiophene homopolymers, although their performance is far from the champions of other classes of LEP.

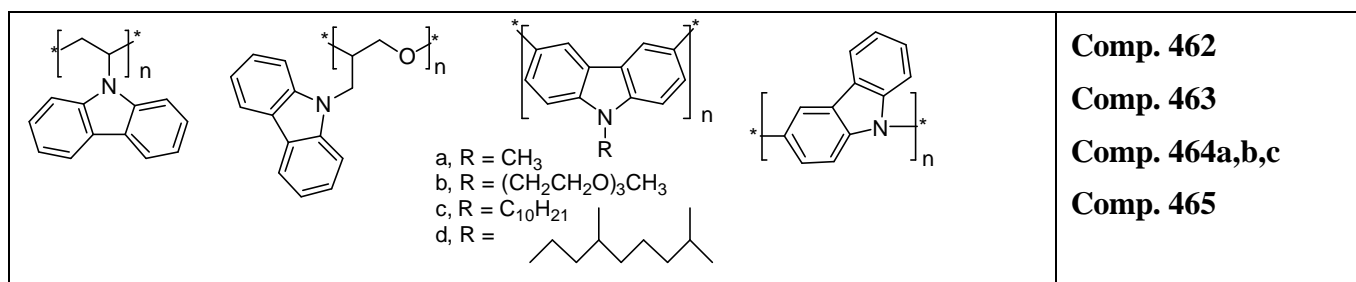
On the other hand, very respectable performance have been demonstrated by blends of PT with other emitting polymers, as exemplifies by a yellow-emitting blend of LPPP **Comp. 524b** with **Comp. 388** (external Q.E. of 4.2%).⁵⁰⁴ Furthermore, easy functionalization of the thiophene nucleus and its electron rich character make it attractive for design of various copolymers with other classes of aromatics/heteroaromatic systems allowing tuning the energy of EL emission and hole/electron transport properties of the materials. In fact, many of the best-performing LEP contained certain amount of thiophene co-monomer units in the structure (e.g., pure red emitter **Comp. 335**⁴⁰³).

4. Miscellaneous classes of light-emitting polymers.

In the previous sections we described three main classes of LEP: PPV, PF and PTs, although many other conjugated and non-conjugated polymers have also been used as EL materials for LEDs. Without making an attempt to cover all types of polymers ever used as electroluminescent materials, below we describe the most important classes and the most prominent examples of EL polymers, not covered in the previous sections. Some more examples of such systems can be found in recent reviews on blue light-emitting polymers²²¹, polycarbazoles,⁵⁵³ and general topic of organic electroluminescent materials.^{20,6,10}

4.1. Carbazole-containing polymers

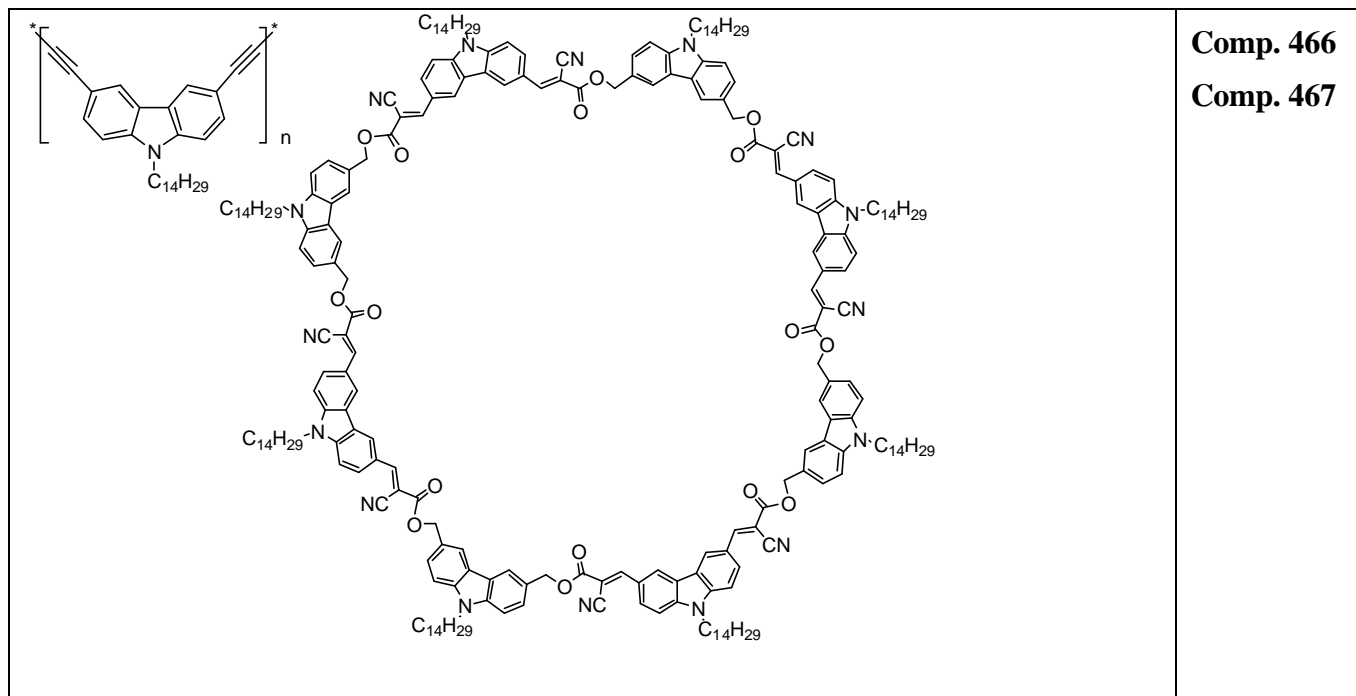
A high hole mobility and excellent photoconductive properties of carbazole-containing polymers, such as poly(*N*-vinylcarbazole) (PVK, **Comp. 462**) and poly(*N*-epoxypropylcarbazole) (PEPK, **Comp. 463**) put them among the most studied polymers for optoelectronic application. They have been commercialized in a number of devices and processes (photocopiers, laser printers, holographic security stamps, etc.).⁵⁵³ The first application of carbazole-containing polymer (PVK **Comp. 462**) in electroluminescent device was described in 1983 by Partridge, although the reported blue EL was due to molecular fluorescent dyes, incorporated into a PVK matrix.² In 1994 Karasz et al. reported blue electroluminescence from pure PVK material (devices ITO/PVK/Ca and ITO/PVK/Al) as well as from a mixture of PVK with PPV block co-polymer **Comp. 163b**.¹⁹⁶ Using PBD/PMMA blend as an additional ETL, a brightness of 200 cd/m² was achieved. Generally, the electroluminescent properties of non-conjugated carbazoles are quite poor. On the other hand, being an excellent hole-transporting material, PVK has been extensively used as a HTL^{102,211,356,373-375} or as a hole-transporting material in blends with other conjugated EL materials in PLEDs.^{390,500,523} **Chapter 7** of this book gives many examples of PVK as a host material for high efficiency phosphorescent PLEDs, using organometallic phosphorescent dopants.



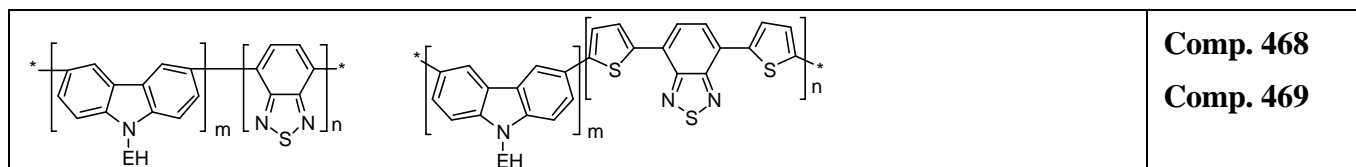
Several carbazole homopolymers (**Comp. 464a**,⁵⁵⁴ **Comp. 464b**,⁵⁵⁵ **Comp. 464c,d**,⁵⁵⁶ and **Comp. 465**⁵⁵⁷) have been synthesized as blue fluorescent materials. The PL maxima of **Comp. 464c** in solution is ~420 nm and it shift to ~490 nm in films.⁵⁵⁶ A blue emitting single layer LEC (λ_{EL} ~ 440 and 490 nm) with external Q.E. of 0.02% was reported for polymer **Comp. 464b**.⁵⁵⁵ Interestingly, mixing **Comp. 464b** with polyquinoxaline (**Comp. 565b**) results in emission of a new color, which corresponds to an energy difference between the LUMO of polyquinoxaline and the HOMO of polycarbazole. A significantly improved external Q.E. of the LEC (1%) was demonstrated with this polymer blend material.⁵⁵⁵

3,6-Carbazole-diacetylene co-polymer **Comp. 466** was used as a hole-transporting layer in bi-layer device with macrocyclic carbazole oligomer **Comp. 467**, which acted as an electron-transporting and light-emitting material.⁵⁵⁸ Co-polymer **Comp. 466** itself is a blue-emitting material (λ_{PL} = 400 nm),

whereas the oligomers **Comp. 467** reveals green fluorescence with $\lambda_{\text{PL}} = 520$ nm. Quite remarkably, octameric cyclic oligomer **Comp. 467** could be prepared in 45% yield by simple Knoevenagel coupling of carbazole-3,6-dicarbaldehyde with 3,6-bis(cyanoacetoxymethyl)carbazole. The PLED fabricated as ITO/**Comp. 466**/**Comp. 467**/Al demonstrated external Q.E. of 0.44 %, although the device maximal brightness was rather low (60 cd/m²).

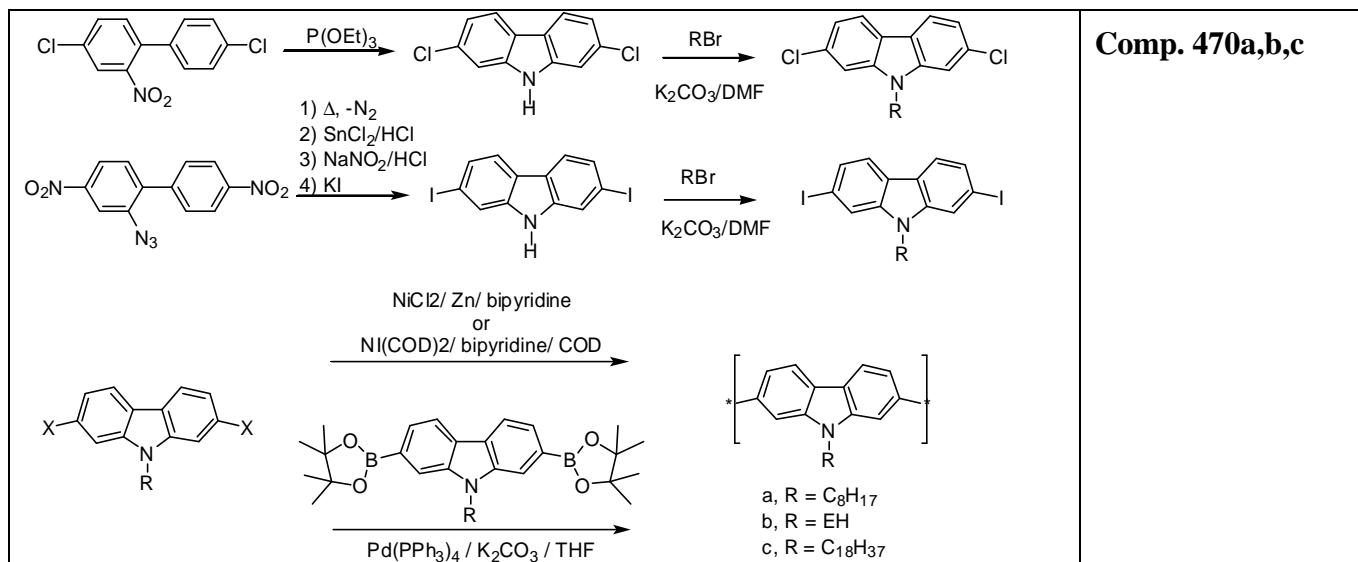


Cao et al. prepared random 3,6-carbazole-benzothiadiazole co-polymers **Comp. 468** and **Comp. 469** by Suzuki coupling.^{559,560} PL and EL emissions of the carbazole segment were completely quenched for co-polymers with benzothiadiazole concentrations as low as 1%, showing an efficient energy transfer on the narrow-band-gap benzothiadiazole sites. Co-polymers **Comp. 469** emitted a saturated red light (from 660 to 730 nm depending on the stoichiometry) with a luminance of 70–631 cd/m² and external Q.E. of 0.55–1.48 %. Also, very high efficiency red-emitting PLED ($\lambda_{\text{EL}} = 680$ nm; CIE: $x = 0.67$, $y = 0.33$) was fabricated by blending small amounts of **Comp. 469** (m:n = 4:1) into MEH-PPV. The device ITO/PEDOT/MEH-PPV:**Comp. 469** (240:1)/CsF/Al showed external Q.E. of 3.8%.⁷² The emission of co-polymers **Comp. 468** was hypsochromically shifted to 570–620 nm and showed a lower $\Phi_{\text{EL}}^{\text{ex}} \sim 0.01$ –0.48 %.



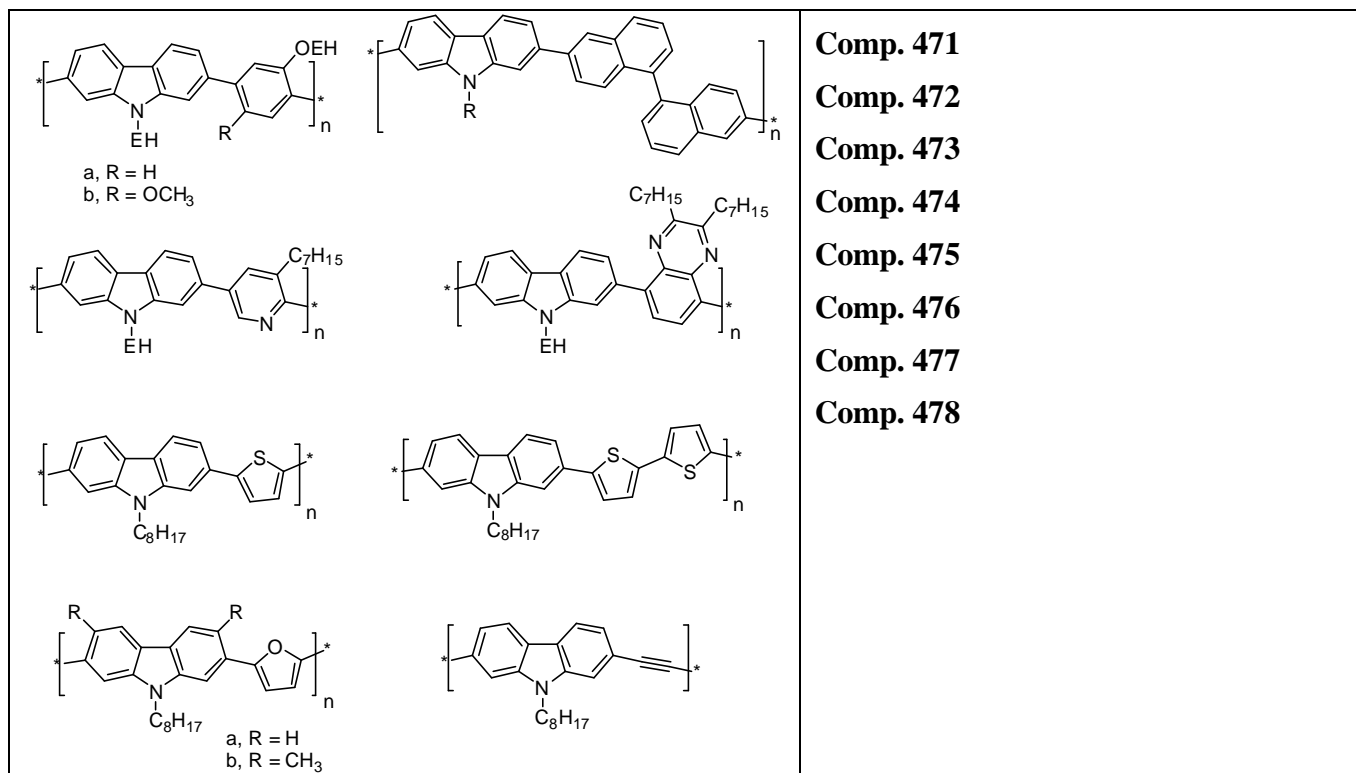
It is noteworthy that the polymer linking via 3,6-positions of the carbazole ring hinders the conjugation due to a “meta-type” connection. The poor conjugation might be responsible for low PL quantum yield of polymers **Comp. 464** (15% for **Comp. 464b** in THF solution). On the other hand, functionalization of carbazole in positions 2 and 7 is a synthetically challenging task. In contrast to fluorene, electrophilic halogenation of carbazole occurs exclusively at positions 3,6 (and then at 1,8) due to strong para/ortho-orientation effect of the nitrogen atom. To prepare fully conjugated

polycarbazoles, Leclerc et al. synthesized 2,7-dihalocarbazoles via reductive cyclization of 4,4'-dichloro-2-nitrobiphenyl (in refluxing triethylphosphite) or thermal decomposition of 4,4'-dinitro-2-azidobiphenyl (followed by multistep converting of the nitro-groups into iodine substituents) (Scheme 68). The polymerized was performed by Yamamoto or Suzuki protocols to afford conjugated polymers **Comp. 470a-c**.^{339,533} In contrast to 3,6-linked polycarbazoles **Comp. 464**, polymers **Comp. 470** showed pure blue emission [λ_{PL} (CHCl₃) = 417–420 nm, λ_{PL} (film) = 439–442 nm] with high PL quantum yield of 76–80 % (in solution). For **Comp. 470**, a blue-emitting PLED has been fabricated, although the initial device testing showed a rather low performance (maximal brightness below 100 cd/m²).³⁴⁰

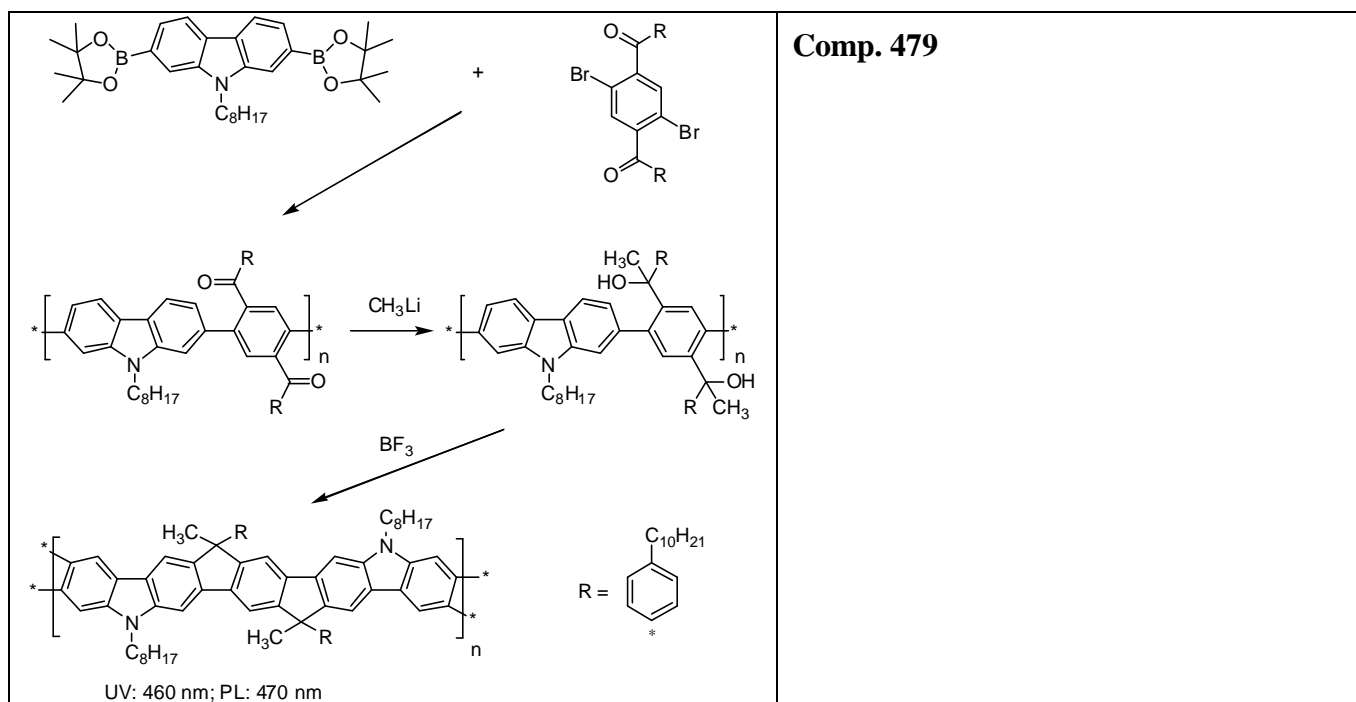


Scheme 68. Synthesis of 2,7-dihalocarbazole monomers and their polymerization by Yamamoto and Suzuki protocols.

As demonstrated in previous sections, carbazole unit was introduced (as a pendant group or as a chain member) in major classes of EL polymers, as PPVs (**Comp. 95–Comp. 105**, **Comp. 138**, **Comp. 169**, **Comp. 182**) and PFs (**Comp. 62**, **Comp. 63**, **Comp. 237–Comp. 240**). A variety of 2,7-carbazole-derived polymers with different conjugated units, such as 2-alkoxy- and 2,5-dialkoxy-1,4-phenylene (**Comp. 471**) and 1,1'-binaphthalene-6,6'-diyl (**Comp. 472**),⁵⁶¹ 2,5-pyridine (**Comp. 473**), 2,7-fluorene (**Comp. 240**)^{339,340} and 2,5'-bithiophene (**Comp. 476**),³³⁹ 5,8-quinoxaline (**Comp. 474**), pentathiophene-*S,S*-dioxide (**Comp. 442**),⁵³³ 2,5-thiophene (**Comp. 475**), 2,5-furan (**Comp. 477**) and acetylene (**Comp. 478**),⁵⁶² was reported by Leclerc et al. Taking advantage of a wide range of electronic properties of the co-monomers, an efficient tuning of the HOMO/LUMO energies and the emission color was achieved in this series.



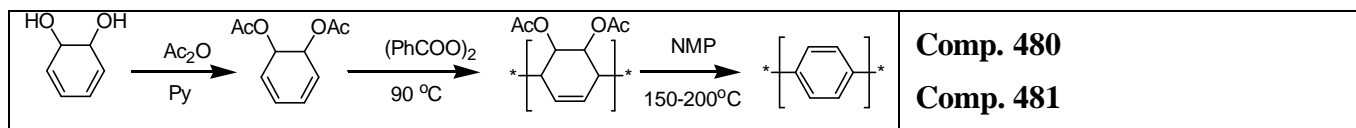
An interesting hydride carbazole-fluorene ladder polymer **Comp. 479** has been recently synthesized by Scherf et al. via Suzuki coupling of carbazole-diboronic ester with dibromodibenzoylbenzene followed by transformation of ketone into alcohol and Lewis-acid catalyzed cyclization (Scheme 69).⁵⁶³ Upon photoexcitation **Comp. 479** emits blue light ($\lambda_{PL} = 470$ nm) with very low Stock-shift (10 nm, 0.057 eV), expected from its rigid geometry. The photophysical studies suggest nearly defect-free intrachain structure of this material, although practical applications of **Comp. 479** in LED are still to be explored.



Scheme 69. Synthesis of ladder-type polycarbazole **Comp. 479**.

4.2. Poly-*p*-phenylenes (PPPs).

The material instability is one of major limitations of the polymer LEDs. In this light, a very high thermal stability of polyphenylenes combined with high PL quantum yield, renders them as attractive materials for device applications. The first PPP-based PLED was described by Leising et al. in 1992.^{564,565} The polymer **Comp. 481** was synthesized by aromatization of a soluble precursor **Comp. 480** (Scheme 70). Owing to relatively high band-gap of PPP **Comp. 481** (2.7–3.0 eV), the PLED ITO/**Comp. 481**/Al emitted blue light with $\lambda_{\text{EL}} \sim 460$ nm (external Q.E. of 0.01%, turn-on voltage of 10 V).⁵⁶⁵ However, high-efficiency EL was never reported for this particular polymer, which might be due to intrinsic defects in the structure (~15% of meta-linkage) associated with the synthetic method.



Scheme 70. Synthesis of PPP by soluble precursor way.

A considerable interest was due to solution-processable PPP materials, prepared by introducing long solubilizing substituents into benzene rings of PPP backbone (**Comp. 482**–**Comp. 484**). Synthesis of such systems was typically achieved via Ni-catalyzed Yamamoto coupling of benzene-1,4-dihalogenides or Pd-catalyzed Suzuki coupling of halogenides with boronic acids or esters, both of which delivered well-defined polymers with molecular weight of $\sim 10^4$.^{566,567, 568} Numerous substituted PPPs, including dialkyl (**Comp. 482a,b**⁵⁶⁷ and **Comp. 484**⁵⁶⁸), alkoxy (**Comp. 482c-e**⁵⁶⁹ and **Comp. 482f-h**⁵⁷⁰), benzoyl (**Comp. 482i**⁵⁷¹) and dialkoxy (**Comp. 482j**,⁵⁷² **Comp. 482k**,⁵⁷³ **Comp. 482l**,⁵⁷⁴ **Comp. 482m**⁶³) PPPs have been synthesized and studied in PLEDs.

Steric hindrance due to alkyl substituents increases the torsion angle between phenylene units which results in additional (unwanted) increase of the band gap. Consequently, the emission band is shifted into the violet region of the spectrum ($\lambda_{\text{PL}} \sim 400$ nm).⁵⁷⁵ The hypsochromic shift due to less sterically demanding alkoxy group is less dramatic ($\lambda_{\text{EL}} = 420$, with much weaker bands at ~ 500 nm and ~ 600 nm) and these polymers show quite high solid state PL quantum yield (35–45%).⁵⁶⁹ Although a relatively poor EL performance (external Q.E. 0.15%, brightness 30 cd/m²) was reported by Chen et al. for alkoxy derivatives **Comp. 482f-h**,⁵⁷⁰ Heeger et al. succeeded in fabrication of the very efficient violet-blue-emitting PLEDs with alkoxy PPPs **Comp. 482c-e**.^{569,576} External Q.E. of 1.8% was reported for the single layer device ITO/**Comp. 482c**/Ca,⁵⁷⁶ and it can be further increased to 3% using a second HTL (in devices ITO/PPV **Comp. 1**/**Comp. 482c**/Ca⁵⁷⁶ or ITO/PVK/**Comp. 482c**/Ca⁵⁶⁹). A ~ 5 times lower efficiency was obtained using a high work-function electrode (Al). Somewhat lower but also very respectable efficiencies were demonstrated by PLEDs with other two alkoxy-PPPs: ITO/PVK/**Comp. 482d**/Ca (2%) and ITO/PVK/**Comp. 482e**/Ca (1.4%).⁵⁶⁹

A second alkoxy substituent in PPP may increase the chain twisting and further enlarge the band gap. Thus, the band gap of 3.4 eV and photo/electroluminescent maxima at ~ 400 nm and ~ 500 nm have been reported for polymer **Comp. 482k**, synthesized by oxidative (FeCl₃) polymerization of di(heptoxy)benzene.⁵⁷³ On the other hand, this could be an effect of defective polymer structure (obtained in oxidative method), as the PL maximum of 435 nm was reported for dibutoxy-PPP **Comp. 482j**.⁵⁷² Blending the later with PVK **Comp. 462** (10%) and PBD **Comp. 21** (10%) to improve the charge-transport properties of the material, a very efficient (external Q.E. 1.2%) PLED was fabricated

with a stable Al cathode, but the reported turn-on voltage was high (20V). In 1995 Heeger et al. have used the dialkoxyPPP **Comp. 482m** to demonstrate the idea of LEC, in which the external Q.E. of 2% was achieved with the Al cathode (in device configuration ITO/**Comp. 482l**:PEO:LiOTf/Al, where PEO is polyethyleneoxide).⁶³

The band gap in substituted PPPs can be tuned to some extent by “diluting” the substituted phenylene rings with the unsubstituted. A bathochromic shift of absorption was observed for co-polymer **Comp. 483** ($E_g = 2.95$ eV), as compared to “all-substituted” homopolymer **Comp. 482k** ($E_g = 3.1$ eV).⁵⁷³ Sandwiching this polymer between ITO and Ca electrodes afforded a blue-emitting PLED with external Q.E. of 0.5%. Even a higher efficiency PLED (external Q.E. 2%) was fabricated from PPP alkoxy/alkyl co-polymer **Comp. 484a** when blended with 10% of diheptylphenylene-thienylene co-polymer **Comp. 444** (device ITO/**Comp. 484**:**Comp. 444**/Ca).⁵⁷⁷ Several other PPP homo- and co-polymers **Comp. 484b-e** based on the diheptylphenylene units have been synthesized.⁵⁶⁸

A very different route to soluble PPP derivatives was demonstrated by Yoshino et al. who introduced perfluorinated alkyl substituents into parent PPP **Comp. 481** by reaction with perfluorobutanoyl peroxide.⁵⁷⁸ The resulting modified polymer **Comp. 485** was soluble in common organic solvents and a solution-fabricated PLED ITO/**Comp. 485**/Mg:In emitted blue to green light (depending on voltage) with band half-width of over 200 nm.

The electroluminescent devices based on sulfonated co-polymer **Comp. 486** were reported by Neher et al.⁵⁷⁹ These polyelectrolyte materials are soluble in DMSO (or in mixed solvents, for **Comp. 486c**). The solution PL maximum (400 nm) does not depend on the counter-ion nature, however the electroluminescence maximum is more sensitive to coulombic interactions and can be shifted from ~480–500 nm (for sodium salt **Comp. 486b**) to 454 nm (for the acid **Comp. 486a**). The external Q.E. of the devices, fabricated between ITO and Al electrodes is between 0.5 and 0.8 %. Later, Reynolds et al. reported related polymers **Comp. 487**, **Comp. 488** where the ionic sulfonate substituents are separated from the PPP backbone by an alkoxy chain.⁵⁸⁰ In contrast to **Comp. 486**, these polymers were soluble in water, however, the PLED device fabricated by sandwiching the blend of **Comp. 487** with polyethyleneimine (as a counter-ion source) between ITO and Al electrode showed very low external Q.E. ~ 0.01%.^{580,581} An interesting approach to fabrication of multilayer PLEDs via sequential adsorption of PPP cationic (**Comp. 487**) and anionic (**Comp. 489**) layers from a water solution was demonstrated by Rubner et al.⁵⁸¹ Although the achieved external Q.E. of the device ITO/35 bilayers (**Comp. 487**/**Comp. 489**)/Al was very low (0.002%), the importance of this work is in demonstration of the novel device fabrication method.

<p>a, R = R' = C₆H₁₃ b, R = R' = C₈H₁₇ c, R = H, R' = OC₁₀H₂₁ d, R = H, R' = OEH e, R = H, R' = O(CH₂)₆C(CH₃)₂CN f, R = H, R' = OC₈H₁₇ g, R = H, R' = OC₁₂H₂₅ h, R = H, R' = OC₁₆H₃₃ i, R = H, R' = C(O)Ph j, R = R' = OC₄H₉ k, R = R' = OC₆H₁₃ l, R = R' = OC₇H₁₅ m, R = R' = O(CH₂CH₂O)₂CH₃</p> <p>a, R = H b, R = CH₃ c, R = C₇H₁₅ d, R = OCH₃ e, R = OC₅H₁₁</p> <p>a, Z = H b, Z = Na c, Z = N(CH₃)₃C₁₄H₂₉</p>	<p>Comp. 482a-o Comp. 483 Comp. 484a-e Comp. 485 Comp. 486a-c Comp. 487 Comp. 488 Comp. 489</p>
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In the previous sections we described the effective tuning of EL properties of other classes of LEP (PPV, PF, PT) by introducing the phenylene units into their backbone (e.g., co-polymers **Comp. 123**, **Comp. 266**, **Comp. 267**, **Comp. 285–Comp. 287**, **Comp. 443**, **Comp. 444**, **Comp. 445**).

Likewise, a series of very effective EL materials were designed by separating the oligophenylene ($n = 2\text{--}5$) blocks by ethylene, vinylene or ethynylene units (co-polymers **Comp. 490–Comp. 500**).⁵⁸²

Changing the length of the phenylene block and separating bridges, the polymer absorption (336–406 nm) and PL maxima (401–480 nm) can be varied over a wide range. The solid state PL quantum yield up to 60–70 % was reported for some of these materials. The electroluminescence can be tuned over an even wider range (423–650 nm) in multilayer PLEDs and, varying the polymer composition and the device structure, the PLEDs with *internal* Q.E. up to 4% were engineered (Table 10).

An aggregation-induced quenching was still a problem for several polymers of this series. Thus, relatively low solid state PL quantum yield was observed for rigid polymers with short PPP blocks (9% for **Comp. 491** and **Comp. 492**). The quenching can be suppressed by blending the light-emitting PPP **Comp. 491** with a hole-transporting poly(phenylbiphenylsylene), which resulted in fivefold increase of the PL efficiency.⁵⁸³ A PLED ITO/polymer blend/Al demonstrated external Q.E. of 0.2%, which is up to two orders of magnitude higher than that obtained in a device with a pure polymer **Comp. 491** layer.

Table 10. Tuning the device performance (EL maxima, turn-on field and internal Q.E.) in PPP co-polymers. PPP – **Comp. 481**, P3V – **Comp. 492**, P3/5V – **Comp. 500**, P2V – **Comp. 491**, P3A – **Comp. 496**, P10E – **Comp. 490**, P3VE – **Comp. 494**.^b – no PVK. [ref. 582. © 1996 Amer. Chem. Soc.]

	monolayer (ITO/Pol/Ca)			bilayer (ITO/PVK/Pol/Ca)			triple layer (ITO/PVK/Pol/PBD ^a /Ca)			monolayer (ITO/Pol/Al)		
polymer	λ_{\max} (nm)	onset (MV/cm)	eff (%)	λ_{\max} (nm)	onset (MV/cm)	eff (%)	λ_{\max} (nm)	onset (MV/cm)	eff (%)	λ_{\max} (nm)	onset (MV/cm)	eff (%)
PPP	450	3.2	0.01		1.3	0.16	423	0.44	0.6		1.5	0.01
P3V		0.94	0.04		0.82	0.10	464	0.83	0.4			
P3/5V		1.2	0.24		0.44	0.13	459	0.69	4.0		2.4	0.02
P2V	483	1.3	0.06				486	0.50	2.0 ^b	482	1.7	0.02
P3A		1.0	0.3		0.5	0.2	650					
P10E	452 (400)	1.4	0.1	450	1.5	0.09	450	0.70	1.0	450	2.1	0.10
P3VE				464	0.75	0.15	463	0.54	1.4			0.12

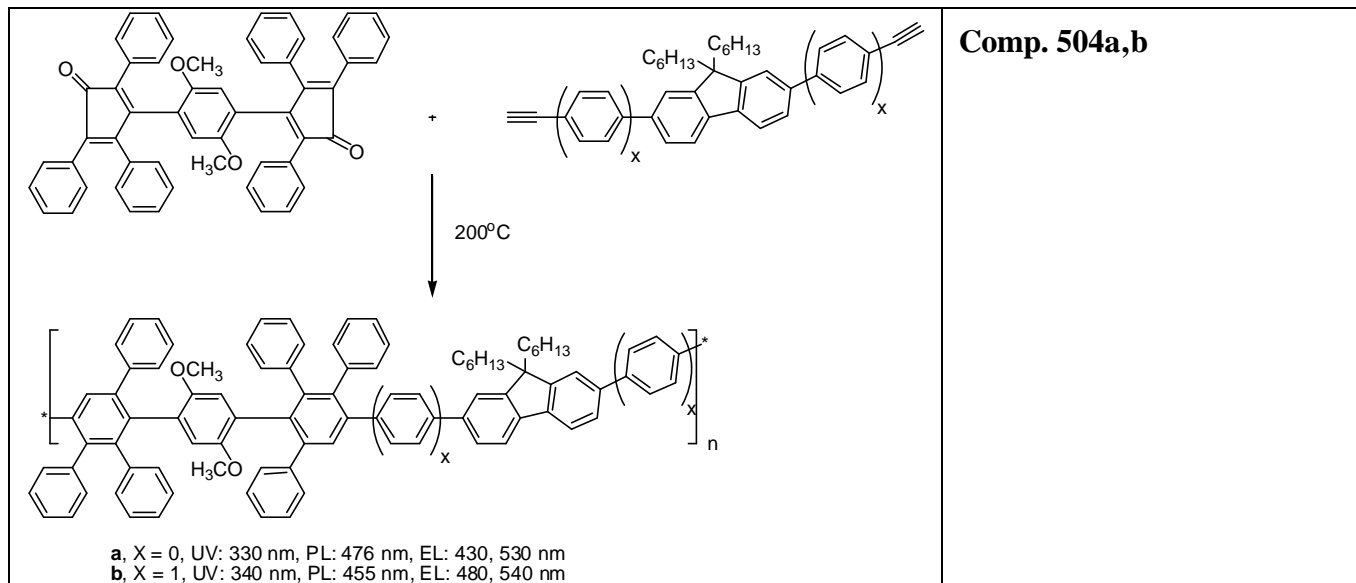
^a) 25% in PMMA matrix; ^b) no PVK layer.

A series of terphenylene vinylene co-polymers **Comp. 501–Comp. 503** was recently synthesized by Ahn, Kwok et al. via Suzuki coupling reaction.⁵⁸⁴ Interestingly, neither alkoxy groups, nor pendant phenyl substituents (attached to vinylene moiety) have any significant effect on the emission properties. The PLEDs fabricated with each of these co-polymers (ITO/polymer/Al) emit blue light with $\lambda_{\text{EL}} \sim 450$ nm (above turn-on voltage of 8–10 V).

	<p>Comp. 490</p> <p>Comp. 491</p> <p>Comp. 492</p> <p>Comp. 493</p> <p>Comp. 494</p> <p>Comp. 495</p> <p>Comp. 496</p> <p>Comp. 497</p> <p>Comp. 498</p> <p>Comp. 499</p> <p>Comp. 500</p> <p>Comp. 501</p> <p>Comp. 502</p> <p>Comp. 503</p>
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A non-common Diels-Alder cyclization polymerization was recently used by Cho et al. for synthesis of sterically hindered co-polymers **Comp. 504a,b**, in which terphenylene or

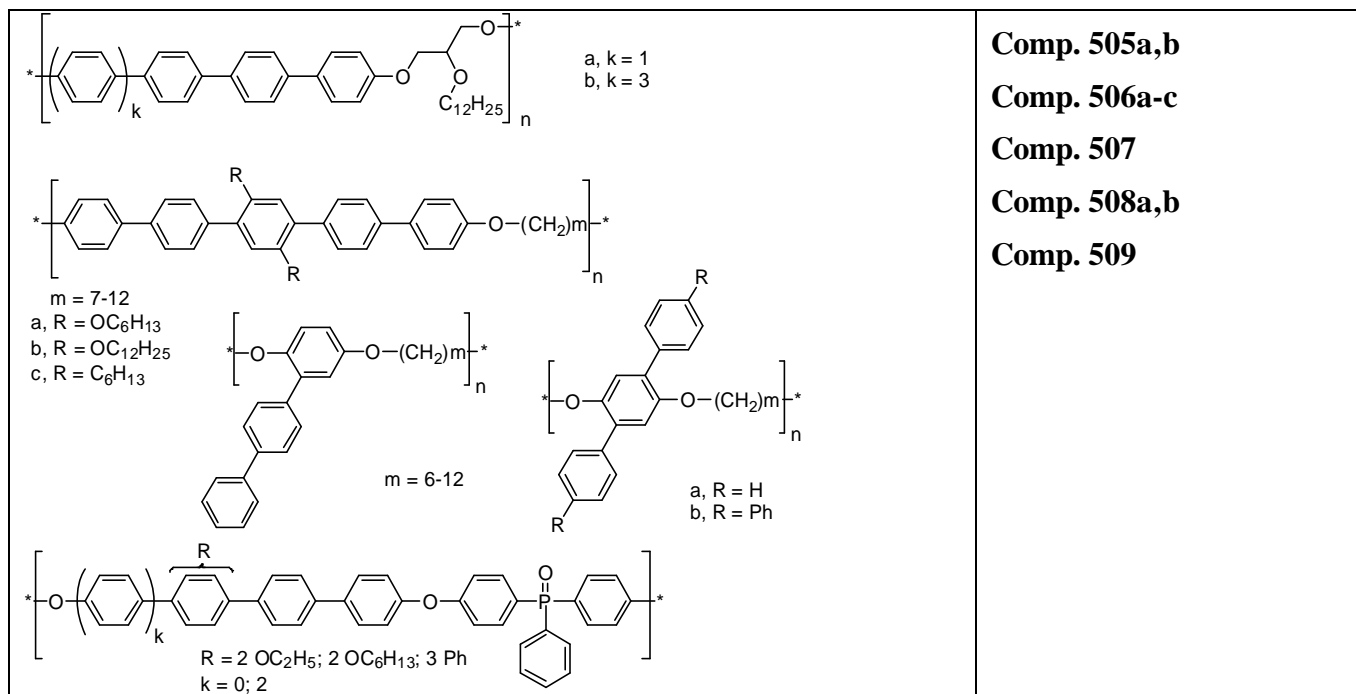
quinquephenylene blocks are separated by dihexylfluorene units (Scheme 71).⁵⁸⁵ Based on the absence of any metal catalyst or initiator in the synthesis, the authors claim this method to be a way to intrinsically high-purity LEPs. However, similar to fluorene homopolymers, the emission of **Comp. 504** in the solid state suffers from a defect-originated (see the PF part) “green band” at ~530 nm, which became more pronounced in EL spectra (the main peak is at ~450–470 nm).



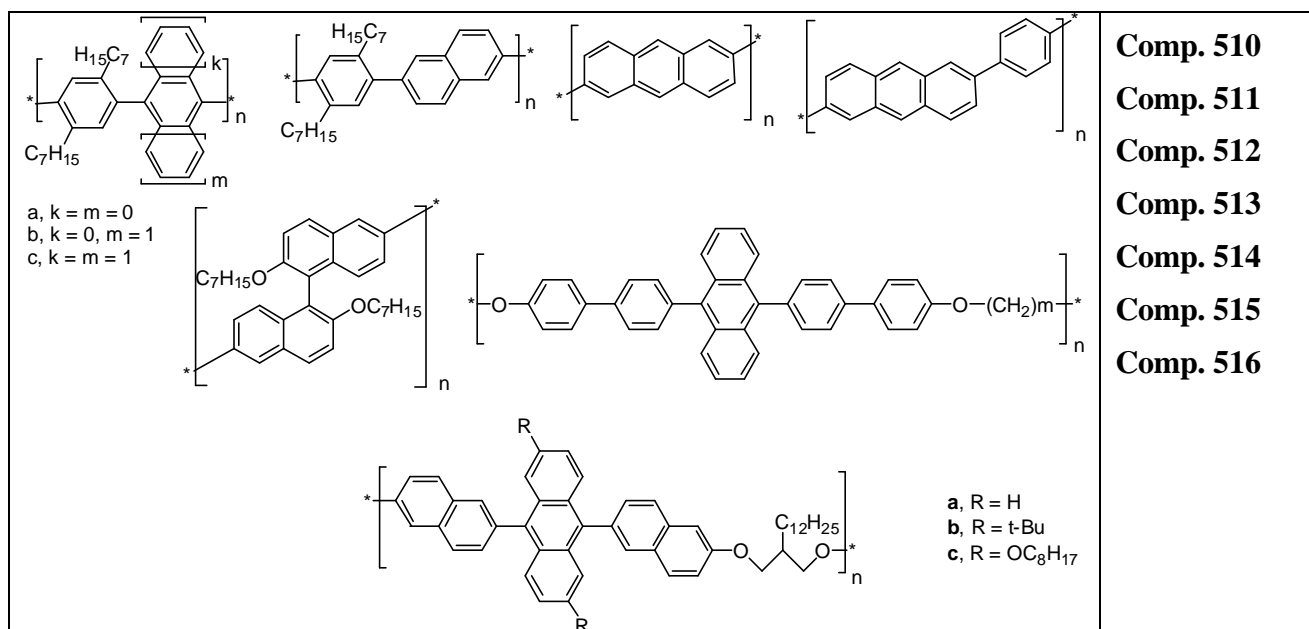
Scheme 71. Synthesis of oligophenylene-fluorene co-polymers via Diels-Alder cyclization.

Scherf et al. reported co-polymers **Comp. 505a,b** containing unsubstituted PPP blocks separated by long-chain-substituted aliphatic blocks.⁵⁸⁶ The compound **Comp. 505a** showed a liquid-crystalline behavior. The PL emission maxima can be tuned by changing the length of the oligophenylene block (396 nm for **Comp. 505a** and 429 nm for **Comp. 505b**). A low efficiency (external Q.E. = 0.05%) PLED was fabricated by blending of a very small amount of **Comp. 505a** into PVK matrix [ITO/PVK:**Comp. 505** (0.045%)/Al].

Later, Kallitsis et al. reported similar PPP co-polymers, with oligophenylene blocks separated by non-conjugated aliphatic chain. Co-polymers **Comp. 506**,⁵⁸⁷ **Comp. 507** and **Comp. 508**⁵⁸⁸ contained the oligophenylene blocks in a main chain or as pendant substituents, respectively. Elongation of the oligophenylene block from terphenylene (**Comp. 507**, **Comp. 508a**) to quinquephenylene (**Comp. 508b**) resulted in a small but observable red shift of PL maxima, from ~390 nm to 407 nm. A somewhat longer wavelength emission was demonstrated by polymers **Comp. 506a,b**, having quinquephenylene blocks in the polymer chain, but introducing the alkyl groups into oligophenylene block (**Comp. 506c**) results in blue-shift of the emission to 372 nm due to the above mentioned steric factor. Related blue-emitting quinquephenylene block co-polymers **Comp. 509** with triphenylphosphino oxide units were reported to have a very high glass-transition temperature (270 °C), but their luminescence efficiency was not investigated in detail.⁵⁸⁹



Several blue-luminescent PPP-type polymers containing naphthalene and anthracene moieties have been synthesized by Suzuki polymerization (**Comp. 510**, **Comp. 511**⁵⁹⁰) and soluble precursor route (**Comp. 512**, **Comp. 513**⁵⁹¹). The anthracene-2,6-diyl polymers **Comp. 512**, **Comp. 513** showed the longest wavelength emission (green-yellow), but no data on the EL performance was reported. Later, Jen et al. reported a very efficient PLED based on polynaphthalene **Comp. 514**.⁵⁹² An orthogonal structure of 1,1'-binaphthyl connection confines the conjugation within the 6,6'-binaphthyl unit, enlarging the band gap of the polymer (3.33 eV) and shifting the fluorescence band into blue region. The PL spectrum of **Comp. 514** is characterized by emission peaks at 390 and 410 nm, and a broad shoulder at 500–600 nm. Only the later is observed in the electroluminescent spectrum ($\lambda_{\text{EL}} \sim 540$ nm), which was attributed to an excimer emission. Alternatively, the higher wavelength emission could be due to planarization of (normally twisted) 6,6'-binaphthyl unit. A device ITO/**Comp. 514**/ETL/Al (ETL – perfluorinated copper phthalocyanine) showed the external Q.E. of 2 % (4.9 lm/W) and attained the maximal brightness of 9,400 cd/m², although the turn-on voltage was rather high (15 V for single layer device and 20 V for double layer with ETL). Anthracene-containing block co-polymers **Comp. 515**⁵⁹³ and **Comp. 516**⁵⁹⁴ have been prepared as highly fluorescent blue-emitting materials. The luminous efficiency of 0.4 cd/A was reported for the device ITO/PEDOT/**Comp. 516b**/Mg:Ag.⁵⁹⁴

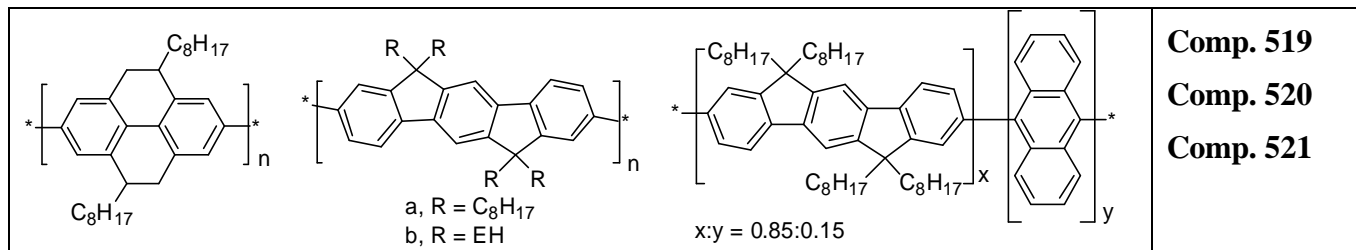


Other light-emitting polycyclic aromatic hydrocarbons (PAH) have also been introduced as pendant groups in non-conjugated polymers, delivering amorphous electroluminescent materials. Thus, blue electroluminescence was recently reported from perylene-containing poly(methylacrylamide) **Comp. 517**.⁵⁹⁵ The PLED fabricated from a blend of **Comp. 517** with charge-transporting polymer **Comp. 518** (ITO/**Comp. 517**:**Comp. 518**/Al) emitted blue light with $\lambda_{EL} = 478\text{--}491\text{ nm}$ (depending on the polymers ratio) and showed a moderate maximal brightness of 500 cd/m^2 (at 15V) but rather low external Q.E. ($\sim 0.01\%$).

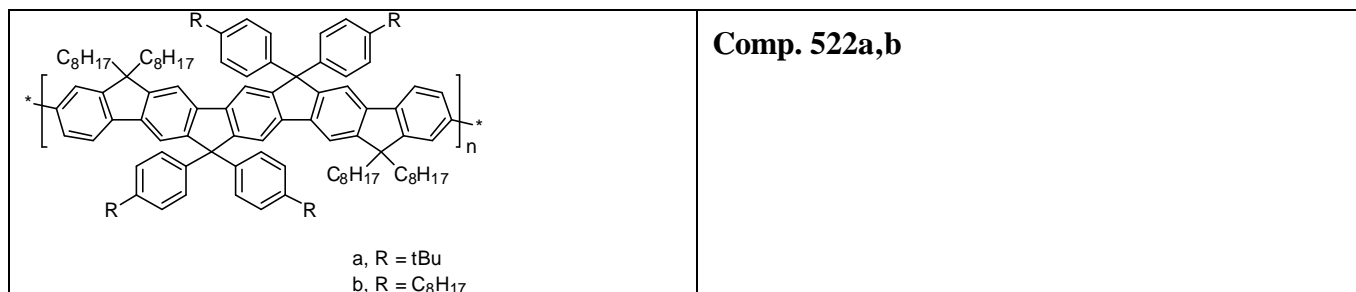


Generally, the fluorescence wavelength and the quantum yield of PPP polymers are very sensitive to the dihedral angle between the phenylene units in the chain. As the energy barrier of this rotation is low, the PL (and EL) maxima depend on the film fabrication conditions. This ambiguity can be eliminated by designing the polymer where the phenylene rings are fixed at a certain angle. Prominent examples of such systems, where the phenylene units are bound in fully planar pairs are PF materials discussed above. In 1995 Müllen et al. reported poly(tetrahydropyrene) **Comp. 519**.⁵⁹⁶ The six-member unsaturated cyclic bridges fix the biphenylene pairs at dihedral angle of $15\text{--}20^\circ$, which is higher than that in PFs ($\sim 0^\circ$) but somewhat lower than in other PPP (23° for unsubstituted **Comp. 481**). In contrast to PPP, the ethylene bridge offers an opportunity to introduce solubilizing substituents into the polymer **Comp. 519** without affecting the dihedral angle and, thus, the emission properties could remain constant ($\lambda_{PL} = 425\text{ nm}$ in solution, 457 nm in films). In this line, the same group later reported

a poly(indenofluorene) **Comp. 520** with three phenylene units being planarized ($\lambda_{\text{PL}} = 432 \text{ nm}$).⁵⁹⁷ This indenofluorene unit was also exploited in Yamamoto synthesis of random indenofluorene-anthracene co-polymer **Comp. 521**, which emitted deep-blue color ($\lambda_{\text{PL}} = 435 \text{ nm}$; CIE: $x = 0.21$, $y = 0.23$) and demonstrated significantly higher color stability (in solid state PL and EL experiments) as compared to homopolymer **Comp. 520**.⁵⁹⁸



As the next step in this way Müllen et al. have recently reported PPP-type polymers **Comp. 522**, containing planar pentaphenylene blocks. As expected, the emission maximum ($\lambda_{\text{PL}} = 445 \text{ nm}$) of **Comp. 522** was found between those of indenofluorene **Comp. 520** (432–434 nm) and completely planar ladder-type PPP (450 nm) (see next section).⁵⁹⁹ Single-layer PLEDs ITO/PEDOT/**Comp. 522b**/Ca/Al showed stable pure-blue emission with brightness in excess of 200 cd/m² (at 7 V).



4.3. Ladder type PPPs.

An ultimate correction of the intrachain dihedral angle was achieved in ladder-type PPP polymers (LPPP), first synthesized by Scherf and Müllen (**Comp. 523**, **Comp. 524**).⁶⁰⁰ The synthesis of these and other types of conjugated ladder polymers has been reviewed by Scherf and Müllen in 1992⁶⁰¹ and more recently, by Scherf.⁶⁰² Due to planarization of the backbone, the band gap of LPPP is decreased to 2.6 eV, and the solution emission maximum is shifted to ~450 nm. The first LPPP-based electroluminescent device was reported by Leising and Grem for polymer **Comp. 523b** using Al, Ca and In anodes and ITO as a cathode.⁶⁰³ The EL spectra confirmed the tendency of the LPPP to aggregation in the solid state, which resulted in yellow emission color. Considering that blue-light EL was one of the objectives for exploration of PPP-type materials, this tendency of a red-shift of the EL maxima stands up as a major obstacle. The early studies claimed the excimer formation (rather than ground-state aggregates) as an origin of the low-energy emission.⁶⁰⁴ On the other hand, in the light of recent findings that ketone (fluorenone) defect quenching is responsible for the red-shift of the emission in PF polymers (see also the PF section),^{289,290} the same mechanism of blue-emission quenching can be anticipated for LPPP materials.²⁹⁰ This is particularly true for polymer **Comp. 523a**, because the hydrogen-terminated methylene bridge in this compound should be more sensitive to oxidation. In fact, it was shown that replacing the hydrogen atom in the methylene bridge with CH₃ reduces the luminescence quenching in the solid state [*cf.* **Comp. 523b**: $\Phi_{\text{PL}} = 72\%$ (in solution) and

10% (in films); **Comp. 524b**: $\Phi_{\text{PL}} = 84\%$ (in solution) and 24% (in films);²⁸⁹ Φ_{PL} as high as 40% for **Comp. 524b** in films was claimed later⁶⁰²]. The long-wavelength emission in both PL and EL spectra of pure **Comp. 524b** in films, although not completely eliminated, was dramatically suppressed as compared to **Comp. 524a**.^{605,606} The problem of low-energy emission in ladder-type PPP was subject of recent studies by UV-vis/IR spectroscopy-assisted annealing experiments, complemented with quantum-chemical calculations. Three types of oxidative defects (ketonic, phenolate and phenol defects) have been discussed as being responsible for the low-energy emission.⁶⁰⁷

Whereas the initial measurements of the freshly fabricated PLED ITO/**Comp. 524b**/Al showed external Q.E. = 0.1%, maturing the device by passing 1 mA current, increases the external Q.E. up to 4% (at 1 μA current). The PLED emitted blue-green light (CIE: $x = 0.23$; $y = 0.33$)⁵⁰⁵ with turn-on voltage of ~ 10 V and maximal brightness of 2,000 cd/m^2 . This record value Q.E. of 4% (as well as typical values of 1.5–2%⁵⁰⁵) for a simple single layer PLED using Al cathode are really outstanding and attracted much attention to this class of LEPs. Other related applications such as polymer lasers,^{608,609} photovoltaics and semiconductors have been also demonstrated for polymers **Comp. 524**.⁶⁰² Recently, the first nanosphere-based PLED was fabricated by spin-coating a water emulsion of **Comp. 524b** (stabilized with PSS) on ITO/PEDOT anode.⁶¹⁰ The device emitted blue-green light with EL efficiency of 0.5 cd/A (with Al cathode) which compares favorably to the efficiency obtained using traditional organic-solution deposition technique (0.3 cd/A in the same device structure).

An efficient white-emitting PLED was fabricated by blending the LPPP **Comp. 524b** with phenyleneethynylene/pyrene co-polymer (**Comp. 535**, see below).⁶¹¹ The blends of blue-emitting **Comp. 524b** with very small amount of red-emitting **Comp. 535** demonstrated efficient energy transfer, emitting rather pure white light (CIE: $x = 0.31$, $y = 0.33$) at all driving potentials. The external Q.E. as high as 1.2% (the highest for a white PLED at that time) was reported for the device ITO/**Comp. 524b**: **Comp. 535**:PMMA/Al. An efficient yellow-emitting PLED was fabricated with **Comp. 524b** by blending in small amounts (1%) of PT **Comp. 388**.^{504,505} The precise emission color of this device can be tuned by adjusting the amount of the PT component, and the external Q.E. as high as 4.2% was achieved. The PLED fabricated under the same conditions with neat **Comp. 524b** showed Q.E. of 2%.

It is noteworthy that lower Q.E. was reported for **Comp. 524b** using a Ca cathode.⁶⁷ The external Q.E. of ITO/**Comp. 524b**/Ca was only 0.4%, although it can be improved to 1.3% by modifying the ITO anode with PANI or SiO_2 nanoparticles layer. For the later, a very high brightness of over 40,000 cd/m^2 was demonstrated.

As mentioned above, in spite of ketone defect origin of the long wavelength emission in PF and related materials, the aggregation is co-responsible for the emission shift in the solid state, because strong inter and intrachain interactions allow an efficient quenching of the excitons in the entire material by a relatively few defect sites. To minimize the formation of the aggregates as observed in fully planar LPPP segmented so-called step-ladder co-polymers **Comp. 525**, where the completely flat LPPP blocks are separated by distorted PPP segments has been designed.^{612,613} Indeed, whereas the synthesized in similar conditions homopolymer **Comp. 523b** reveals a significant red shift of the PL and EL emission maxima when going from a film to a solution, the emission of segmented co-polymer **Comp. 525** stays almost unaltered (Figure 32). Sandwiching **Comp. 525b** between ITO and Al electrodes affords a pure blue-light emitting PLED with average Q.E. of 0.2%.⁶¹²

A significant suppression of the yellow emission band of LPPP was also achieved by dilution in PVK matrix, which also resulted in 2–3 times increase in EL efficiency compared to the device prepared with neat LPPP (ITO/polymer/Al).⁶¹⁴

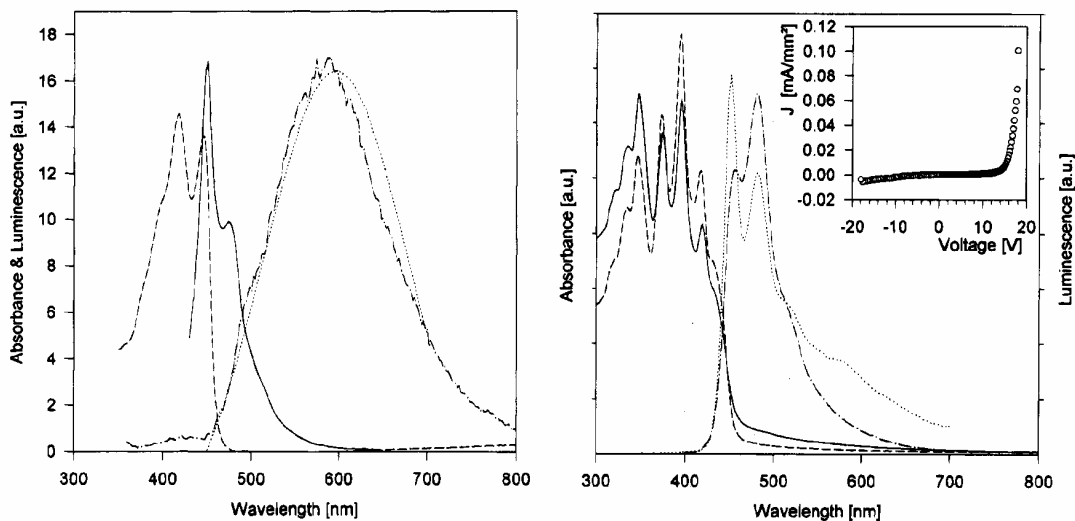
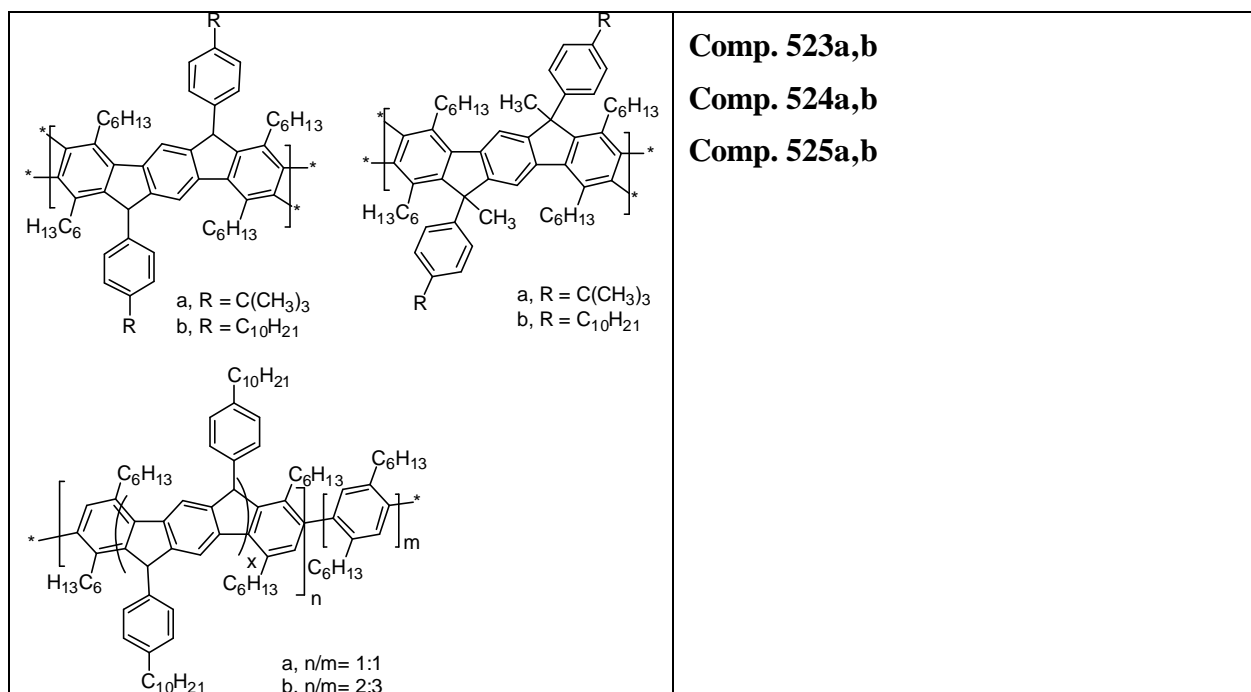


Figure 32. Left: absorption (dashed), solution PL (solid), PL in films (dot-dashed) and EL (dotted) spectra for **Comp. 523b**. Right: absorption spectra of **Comp. 525a** (dashed), **Comp. 525b** (solid); PL (dotted) and EL (dot-dashed) spectra of **Comp. 525b**; inset is *I*-*V* characteristic of ITO/**Comp. 525b**/Al device. [From Ref. 612, © 1995 American Chemical Society].

4.4. Poly(phenylene ethynylene)s.

After the first successful synthesis of soluble poly(phenylene ethynylene) (PPE) derivative by Giesa et al. and elaboration of elegant methods for preparation of different derivatives of this polymer, PPE materials have played important roles in many electronic applications, from sensors and molecular wires to polarized displays.^{615,616,617} The first electroluminescence from poly(phenylene ethynylene) (PPE) was reported in 1993 by Swanson et al. for dialkoxy-PPE **Comp. 526** sandwiched between ITO and Ca electrodes.⁶¹⁸ The polymer **Comp. 526** has low band gap of ~2.25 eV and emits orange-red

light with $\lambda_{\text{PL}} \sim 585$ nm and $\lambda_{\text{EL}} \sim 605$ nm (with a broad tail at ~ 800 nm). A very detailed study of a series of dialkoxyPPE polymers and co-polymers with various alkoxy substituents were conducted by Wrighton et al.^{619,620,621} A PL quantum efficiency of up to 86% and 36% was demonstrated for polymers **Comp. 527** in solution and in films, respectively.⁶²¹ It was demonstrated that the polymer band gap and the emission maxima are shifted from the solution ($E_g \sim 2.6$ eV, $\lambda_{\text{PL}} = 473$ nm) to the solid state ($E_g \sim 2.25\text{--}2.45$ eV, $\lambda_{\text{PL}} \sim 530\text{--}590$ nm). These shifts as well as the observed decrease in the PL quantum yield in films are related to the degree of crystalline order and can be controlled by the substitution pattern. The PLED devices ITO/polymer/Al were reported for co-polymers **Comp. 527** ($R = C_{18}H_{37}$, $R' = \text{EH}$).⁶²² The EL performance of the device with neat polymer was rather low (external Q.E. 0.004%, maximal brightness 4 cd/m²) but it can be essentially improved by blending with poly-TPD hole-transporting material (external Q.E. 0.02%, maximal brightness 146 cd/m²).

Wudl et al. reported epi-cholestanoxo PPE **Comp. 526c**, where the steroid substituents were supposed to preclude the crystallization in the solid state and, therefore, to maximize the PL efficiency.⁶²³ PPEs **Comp. 528**, synthesized by Swager's group contained the triptycene units, which acted as "insulating cover", providing a good separation between the PPE chains.^{624,625} Consequently, the PL spectra in solution and in films were almost identical ($\lambda_{\text{PL}} = 455$ nm). Due to a nanoporous structure, formed by triptycene cavities, polymers **Comp. 528** act as efficient sensors for trinitrotoluene explosive, which is based on quenching the fluorescence of the former by nitroaromatic molecules.⁶²⁴ Targeting at possible biosensor applications, Schanze et al. reported water-soluble PPE polyelectrolyte **Comp. 529**, similar to the PPV-type material **Comp. 142**.⁶²⁶ Changing the solvent from MeOH to water, the aggregation of **Comp. 529** was observed by significant red-shift and broadening of the emission spectrum. The group of Swager reported cyclophane-type PPE **Comp. 530**, for which an interesting aggregation-related phenomenon was observed.⁶²⁷ While the PL of **Comp. 530** in solution and in Langmuir-Blodgett films is featured by a narrow emission band ($\lambda_{\text{PL}} = 470\text{--}480$ nm, band half-width ~ 30 nm) and very low quantum yield (5–6%), aggregation of the polymer in spin-coated films, in contrast to reasonable expectations, increases the quantum yield to 21 % and the aggregate emission is seen as a very wide band ($\lambda_{\text{PL}} = 520$ nm, band half-width ~ 140 nm).

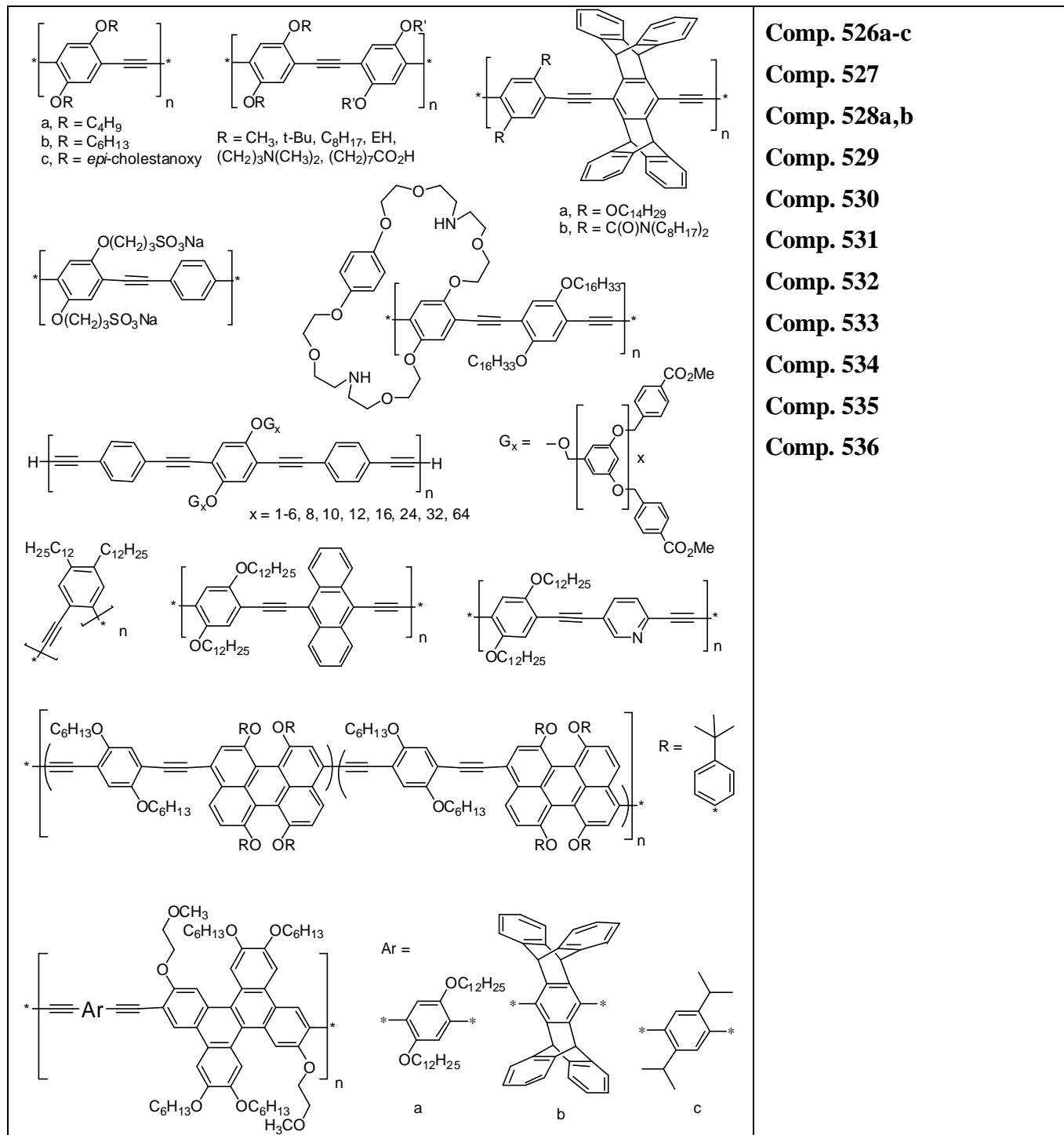
An interesting example of extremely long monodisperse phenyleneethynylene "wires" **Comp. 531**, insulated ("wrapped") by dendritic substituents was recently reported by Jiang, Aida et al.⁶²⁸ For the oligomers with the first generation dendrimer substituents (G_1) the PL quantum yield decreased at increasing "wire" length (n), from 80–90% to below 60%, whereas steadily high (above 80%) Φ_{PL} was observed for all the oligomers containing bulkier G_3 substituents. Furthermore, increasing the concentration of **Comp. 531- G_3** (in THF solution) does not decrease the fluorescence yield, which is in contrast to G_1 -substituted homologues.

The electroluminescent poly(*ortho*-phenylene ethynylene) **Comp. 532** was reported by Onoda et al.⁶²⁹ As expected, the optical band-gap of **Comp. 532** (3.1 eV) is larger than that of para-connected polymer **Comp. 526**, making the former a blue-purple-emitting material ($\lambda_{\text{PL}} \sim 400$). Interestingly, **Comp. 532** possesses a low LUMO energy and can be *n*-doped electrochemically (partially reversible wave at $E_{\text{p.c.}} = -1.2$ V vs. Ag/Ag⁺ [~ -0.9 V vs. SCE]). The PLED ITO/**Comp. 532**/Al emits blue light with two peaks at $\lambda_{\text{EL}} \sim 410$ and 430 nm.

Just as in other conjugated polymers, the emission color of PPE can be tuned by introducing different conjugated fragments in the polymer chain (co-polymers **Comp. 533** and **Comp. 534**).^{619,630} Thus, red-orange EL ($\lambda_{\text{EL}} \sim 590$ nm and a shoulder at 530 nm) was reported for the anthracene-based polymer **Comp. 533** (in PLED ITO/**Comp. 533**/Al), whereas introducing a pyridine moiety into the polymer chain results in significant blue shift of the emission, and a blue-green emitting ($\lambda_{\text{EL}} \sim 480$ nm) PLED was fabricated with this material.⁶³⁰

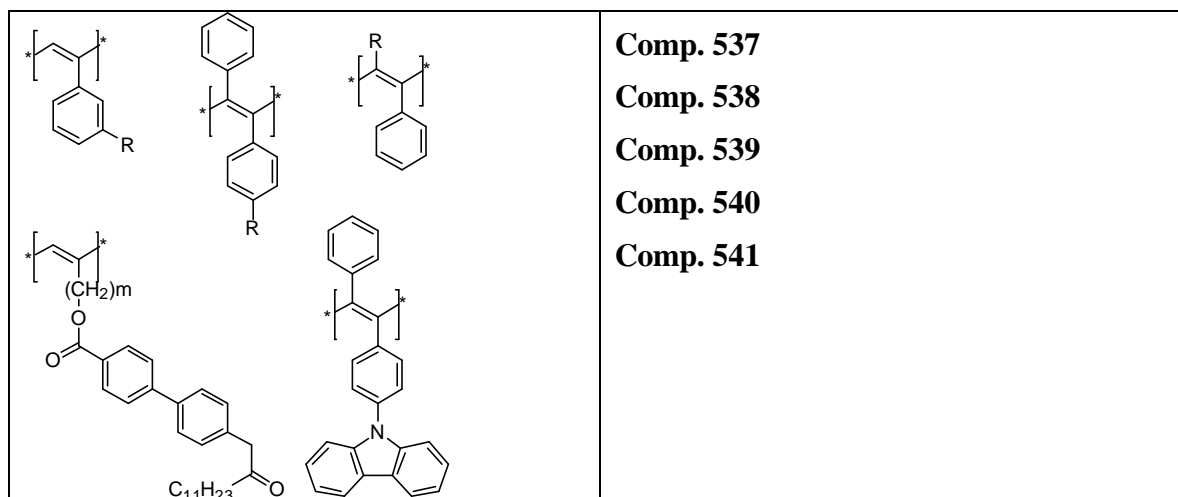
Higher polycyclic aromatic units such as perylene (**Comp. 535**⁶³¹) and dibenzocrysene moiety (**Comp. 536a-c**⁶³²) were introduced into PPE backbone. Interestingly, whereas the former is a red-

emitting materials with $\lambda_{\text{PL}} = 580\text{--}590\text{ nm}$ (which was applied to create white-emitting PLED with LPPP),⁶¹¹ significantly higher energy, blue color emission was observed from the crysene-derivatives ($\lambda_{\text{PL}} = 474\text{--}480$, $\Phi_{\text{PL}} = 25\text{--}34\%$).⁶³² The later were employed as fluorescent sensor materials and demonstrated better sensitivity than other similar iptycene-contained light-emitting polymers (e.g., **Comp. 528**).⁶³²

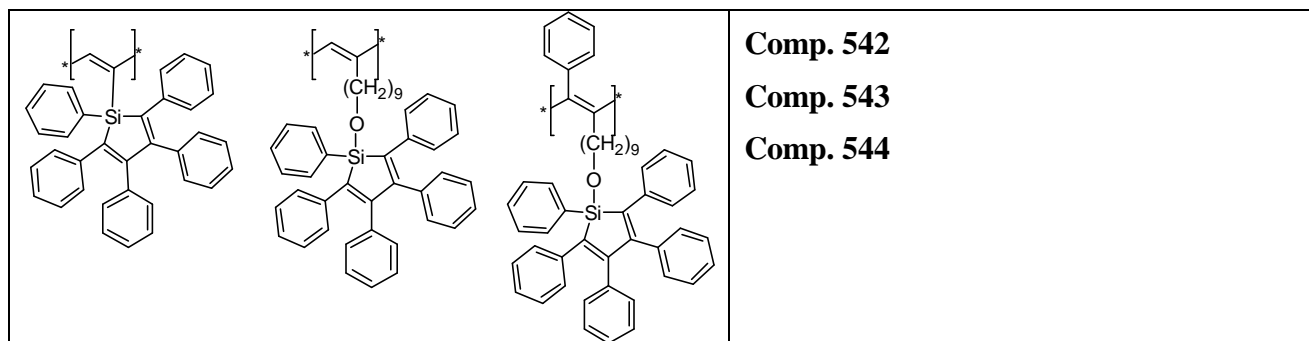


4.5. Substituted polyacetylenes.

Polyacetylene (PA), the first and the most conducting polymer, was traditionally regarded as a non-emissive material. Although it is certainly true for the unsubstituted PA, in both doped and neutral state, strong fluorescence has been recently demonstrated from disubstituted (diphenyl and phenylalkyl) PAs.^{633,634,635} Kobayashi et al. fabricated red, green and blue electroluminescent devices by sandwiching monophenyl-PA (**Comp. 537**), diphenyl-PA (**Comp. 538**) and phenylalkyl-PA (**Comp. 539**), respectively, between ITO and Mg:Al electrodes.⁶³⁴ As expected from a low PL quantum yield (<0.1 %) of monophenyl-PA, efficiency of the red-emitting PLED based on polymer **Comp. 537** was negligibly low ($\sim 10^{-4}$ %). Better results were demonstrated by green (**Comp. 538**) and blue-emitting (**Comp. 539**) disubstituted PAs (external Q.E. ~ 0.01 %), in accordance with their high PL efficiency (>60 %). The structural variations included biphenyl- and carbazole-contained PAs **Comp. 540**^{636,637} and **Comp. 541**⁶³⁸. The former is a UV/violet-emitting material ($\lambda_{\text{PL}} = 350\text{--}370$ nm), where the emitting sites (biphenyl chromophores) are separated from the PA backbone by long alkyl chain. In contrast, strong green fluorescence ($\lambda_{\text{PL}} = 525$ nm) of carbazole-contained **Comp. 541** cannot be attributed to the individual carbazolyl substituents. A remarkably efficient PLED (external Q.E. = 2%, maximal brightness 2,700 cd/m²) was fabricated from **Comp. 541** as a bilayer device ITO/**Comp. 541**/Alq₃/Mg/Al, where Alq₃ acts as an electron-transporting layer and the observed EL is exclusively due to PA material.⁶³⁸

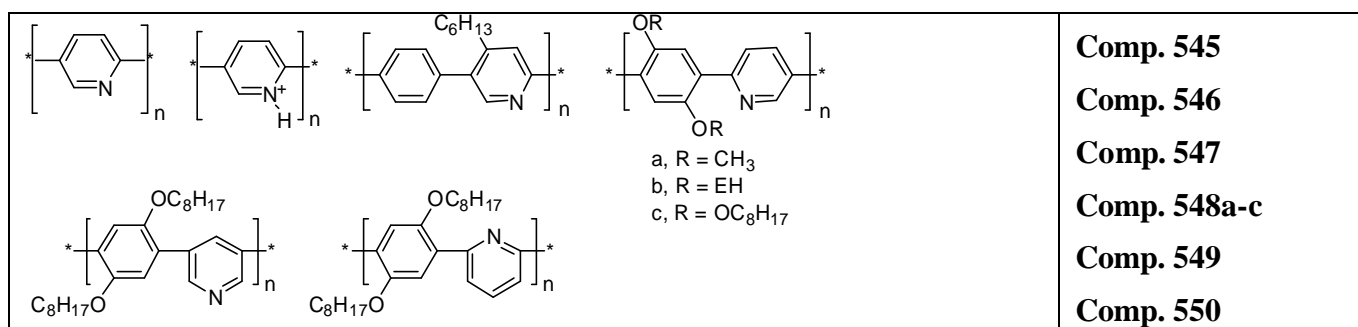


Inspired by very high EL efficiency of OLEDs with molecular siloles, Tang et al. reported an interesting series of silole-substituted PAs **Comp. 542–Comp. 544**.⁶³⁹ Whereas the fluorescence of all three polymers in solution was very low ($\Phi_{\text{PL}} < 0.5$ %), a significant increase of the PL quantum yield (20–50 times) was observed in the solid state of **Comp. 543** and **Comp. 544**. The phenomenon was earlier observed in molecular siloles, as well as in cyclophane-PPE **Comp. 530**. While an efficient energy transfer from silole onto PA backbone renders **Comp. 542** a red-emitting material ($\lambda_{\text{EL}} = 664$ nm), blue-green fluorescence ($\lambda_{\text{EL}} = 512$ nm) was observed in PAs **Comp. 543** and **Comp. 544** with longer bridge between silole and PA backbone. The EL efficiency of single-layer devices with all three polymers was similar (~ 0.013 %), in spite of different PL properties, which suggested the device performance was limited by charge-transport processes. Indeed, multiplayer device ITO/**Comp. 544**:(PVK **Comp. 462**)/BCP/Alq₃/Al emitted blue light ($\lambda_{\text{EL}} = 496$ nm) with relatively high current and quantum efficiencies (1.45 cd/A and 0.55%, respectively), and maximal brightness of 1,118 cd/m².⁶³⁹



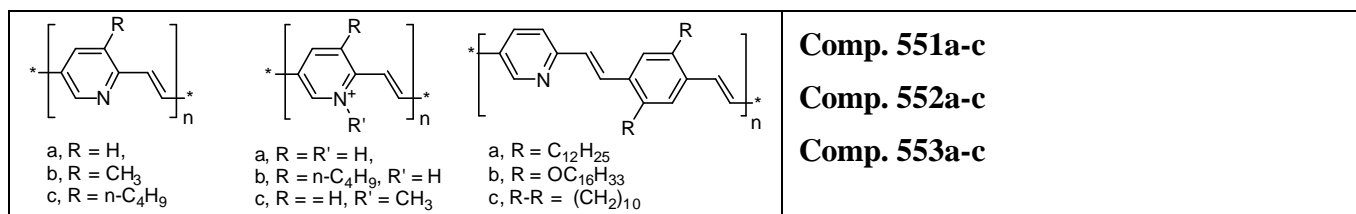
4.6. Poly(pyridine)s and related poly(N-heterocycle)s.

The first electroluminescence from polypyridine was reported by Epstein et al. in 1995.⁶⁴⁰ The polymer **Comp. 545**, prepared by Yamamoto Ni-mediated reductive coupling of 2,5-dibromopyridine⁶⁴¹ was soluble in formic acid (due to formation of a protonated form **Comp. 546**), and thus could be spin-coated on ITO glass substrate for preparation of PLED. The device ITO/**Comp. 545**/Al emitted green light ($\lambda_{EL} \sim 500$ nm) at voltages above 8 V, and introducing an additional HTL (PANI) can reduce the turn-on voltage to 4 V. Unfortunately, the efficiency and the brightness of the device have not been reported. Also, the issue of deprotonation of the pyridine units (which might occur during vacuum deposition of a second electrode) and the possible influence of residual protonated species has not been addressed. Electroluminescent pyridine-phenylene co-polymers **Comp. 547**⁶⁴² and **Comp. 548a-c**⁶⁴³ have been synthesized and studied by Bryce et al. Although a rather low external Q.E. (<0.1 %) was reported for the devices, an interesting phenomenon was found for polymers **Comp. 548a-c**. When the PLED (ITO/PEDOT/**Comp. 548a-c**/Ca/Al) was fabricated using acidic solution of the polymer, a strong red shift in the EL band as compared to that obtained when using neutral solution (from 510 to 575 nm) was observed. The authors explain this by planarization of the protonated polymer chain as a result of intramolecular hydrogen bonding $N \cdots H \cdots O$. Variation of pyridine linkage in co-polymers **Comp. 548a-c**, **Comp. 549** and **Comp. 550** have shown affects on PL and EL emission of materials ($\lambda_{EL} = 444, 432$ and 428 nm, respectively) although the details of the efficiency of fabricated LEDs has not been reported.⁶⁴⁴

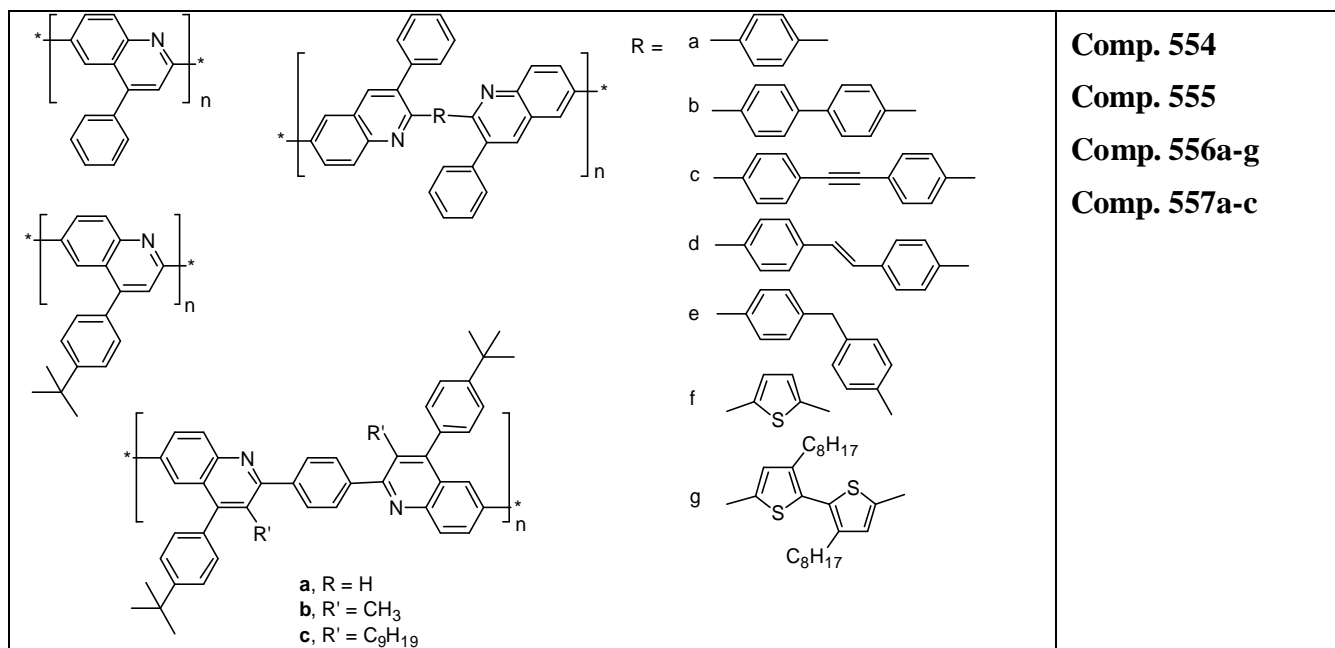


Several poly(*p*-pyridine vinylene)s (PPyV, **Comp. 551**) have been reported as isoelectronic analogs of PPVs.^{645,646,647} Both the neutral and the protonated (**Comp. 552**) forms showed strong luminescence from excimeric states, which contributed to the observed red shift in the emission spectra from solution (from 470 to over 600 nm) and low PL quantum yields. The fabricated ITO/**Comp. 551a-c**/Al device showed an external Q.E. of 0.02 %, which can be somewhat improved to 0.05 % by introducing a HTL of PPV **Comp. 1**.⁶⁴⁷ The efficiency as high as 0.3% was reported for co-polymer **Comp. 553** on bilayer PLED with PANI networked electrode.⁶⁴⁸ Several studies of PPy homo and co-

polymers (**Comp. 545**, **Comp. 551**, **Comp. 553**) as light-emitting materials for symmetrically configured a.c. light-emitting (SCALE) devices⁶⁴⁹ and inverted LEDs⁶⁴⁸ using high work-function electrodes (Au) have been performed.



A solid study of photo- and electroluminescent properties of a series of poly(quinoline) homo- and co-polymers **Comp. 554–Comp. 557** was reported by Jenekhe et al.^{650,651,549} Changing a substituent R' and a co-unit R, the emission color was tuned from blue to red ($\lambda_{\text{EL}} = 410\text{--}622\text{ nm}$) (Figure 33). A solid state PL quantum yield of these polymers was usually on the level of 10 %, although higher efficiency (20–30%) was observed for *tert*-butyl substituted polymers **Comp. 555** and **Comp. 557a**.⁶⁵⁰ The PLED devices fabricated with **Comp. 554–Comp. 557** in ITO/HTL/polymer/Al configuration showed moderately high external Q.E. of ~0.1–1 %, with values repeating the trend of PL efficiencies (the highest external Q.E. = 0.92% and 1.08% were due to polymers **Comp. 555** and **Comp. 557a**, respectively). An emissive polymer **Comp. 556g** showed good electron transport properties and a weak green EL (external Q.E. = 0.06 % in ITO/**Comp. 556g**/Al device configuration). Furthermore, a large improvement in the performance of MEH-PPV based LEDs was observed using the **Comp. 556g** as the electron transport material (external Q.E. = 0.68 % and luminance of 2,311 cd/m²).⁵⁴⁹ Considering relatively low EL turn-on voltage of 5–10 V, these polymers present a promising class of polyheterocyclic materials for LED displays.



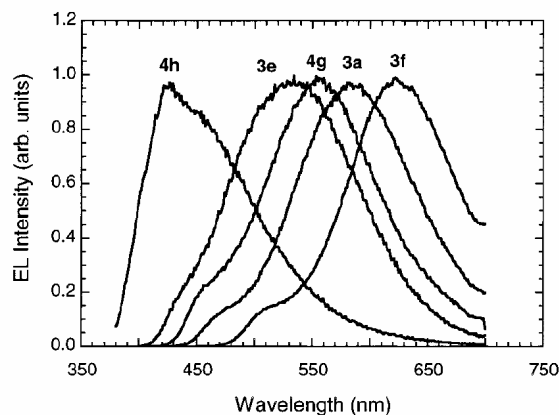
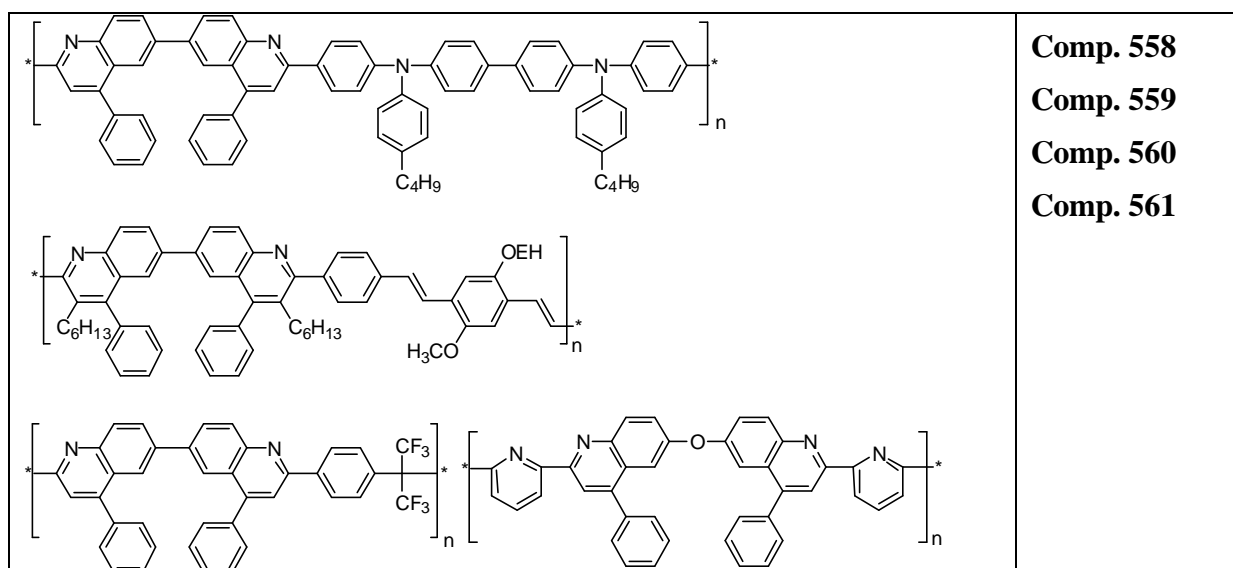


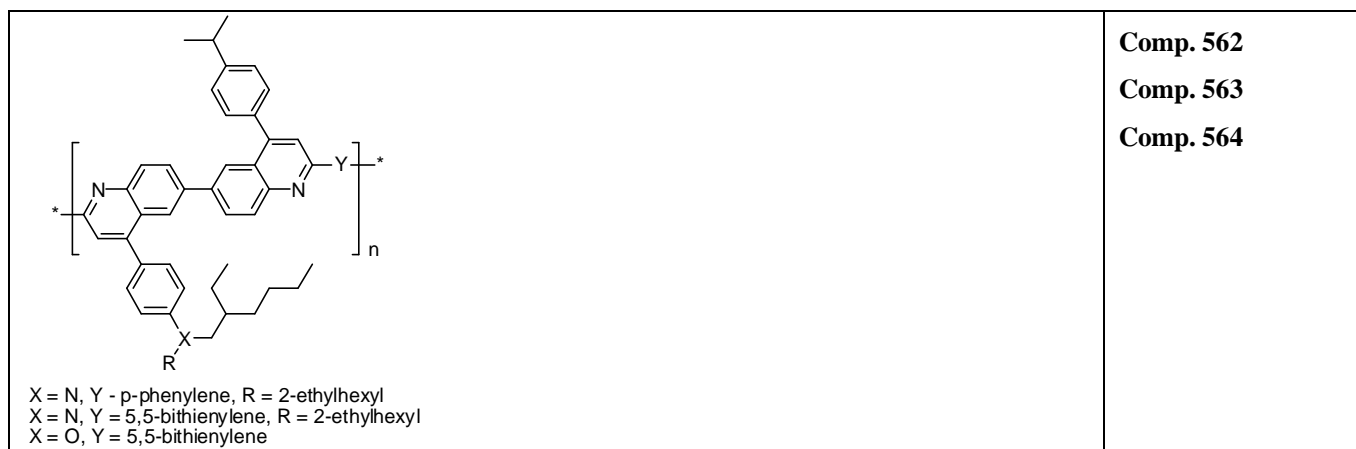
Figure 33. Tuning the electroluminescence color in polyquinoline derivatives (device structure ITO/HTL/EL polymer/Al, where HTL is triarylamine-based molecular material [for polymers **Comp. 556**] or PVK **Comp. 462** [for polymer **Comp. 557**]; 3a – **Comp. 556a**, 3e – **Comp. 556e**, 4g – **Comp. 557a**, 4h – **Comp. 557b**). [From Ref. 650, © 1999 American Chemical Society].

Jen et al. reported PLEDs based on variations of the above mentioned 6,6'-bisquinoline co-polymers (**Comp. 558–Comp. 561**) containing conjugated and non-conjugated linkers.^{652,653} For co-polymers with non-conjugated units the EL efficiency was very low (0.002% for ITO/**Comp. 561**/Al⁶⁵³), although similar value was demonstrated for MEH-PPV in same device configuration. Introducing conjugated arylamine or phenylenevinylene linkers improves the external Q.E. to 0.018% (for triarylamine co-polymer ITO/**Comp. 558**/Al) and 0.06% (for phenylenevinylene co-polymer ITO/**Comp. 559**/Al).⁶⁵² Also, non-conjugated co-polymers **Comp. 560**, **Comp. 561**, which possess relatively high electron affinity, showed lower turn-on voltage (~6 V). Many other quinoline-containing polymers have been used in PLEDs as electron-transporting materials in combination with other EL polymers (e.g., quinoline-containing polystyrene **Comp. 234**, with PFO³³¹).



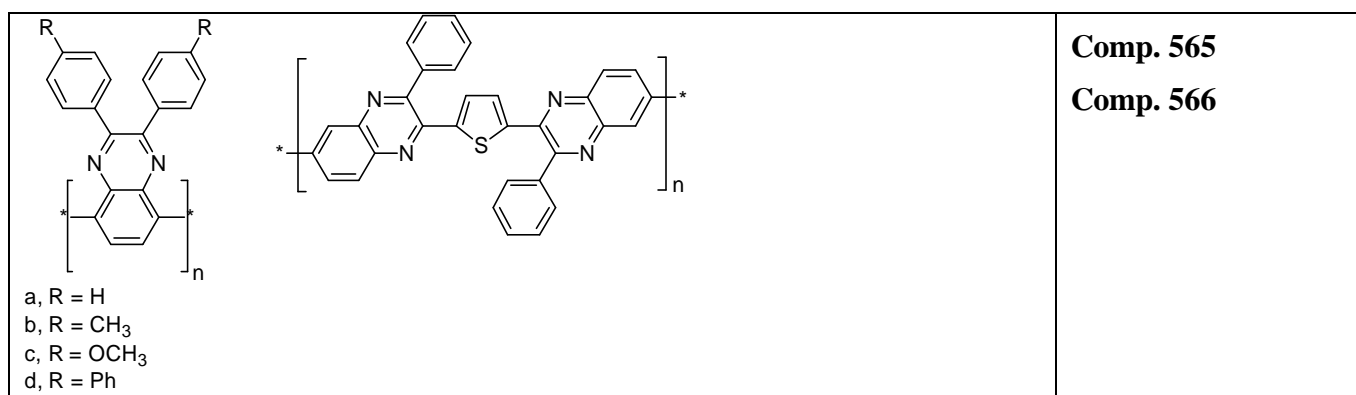
Several other 6,6'-bisquinoline-based copolymers **Comp. 585–Comp. 587** have been reported.⁶⁵⁴ Both absorption and PL spectra of polymers **Comp. 586**, **Comp. 587** containing bithiophene units are red-shifted as compared to the analog with *p*-phenylene fragment **Comp. 585**,

showing broad structureless PL in the films at $\approx 5520\text{--}650\text{ nm}$. Single layer ITO/PEDOT/polymer/Ca/Ag devices fabricated with these polymers showed moderate performance with maximum luminance and maximum brightness of $0.17\text{--}0.58\text{ cd/A}$ and $90\text{--}150\text{ cd/m}^2$, respectively.



In 1996 Yamamoto et al. reported the electroluminescence from related poly(quinoxaline)s **Comp. 565**.⁶⁵⁵ In contrast to unsubstituted polypyridine, all polymers **Comp. 565** appeared to be soluble in organic solvents. For all polymers of the series, both single layer (ITO/polymer/Mg(Ag)) and double layer devices with different HTL emitted green-blue light at $\lambda_{\text{max}} 490\text{ nm}$, but the device brightness was rather low (on the order of $1\text{--}10\text{ cd/m}^2$).

Excellent electron-transporting properties of quinoxaline (also demonstrated for non-conjugated quinoxaline-containing polymer⁶⁵⁶) resulted in substantially decreased turn-on voltage of PPV/**Comp. 566** PLED (3.6 V), which is much lower than that of pure PPV in the same conditions (7 V), and the diode showed maximum luminance of 710 cd/m^2 (ca. 40 times brighter than the PPV diode at the same current density and voltage).⁶⁵⁷

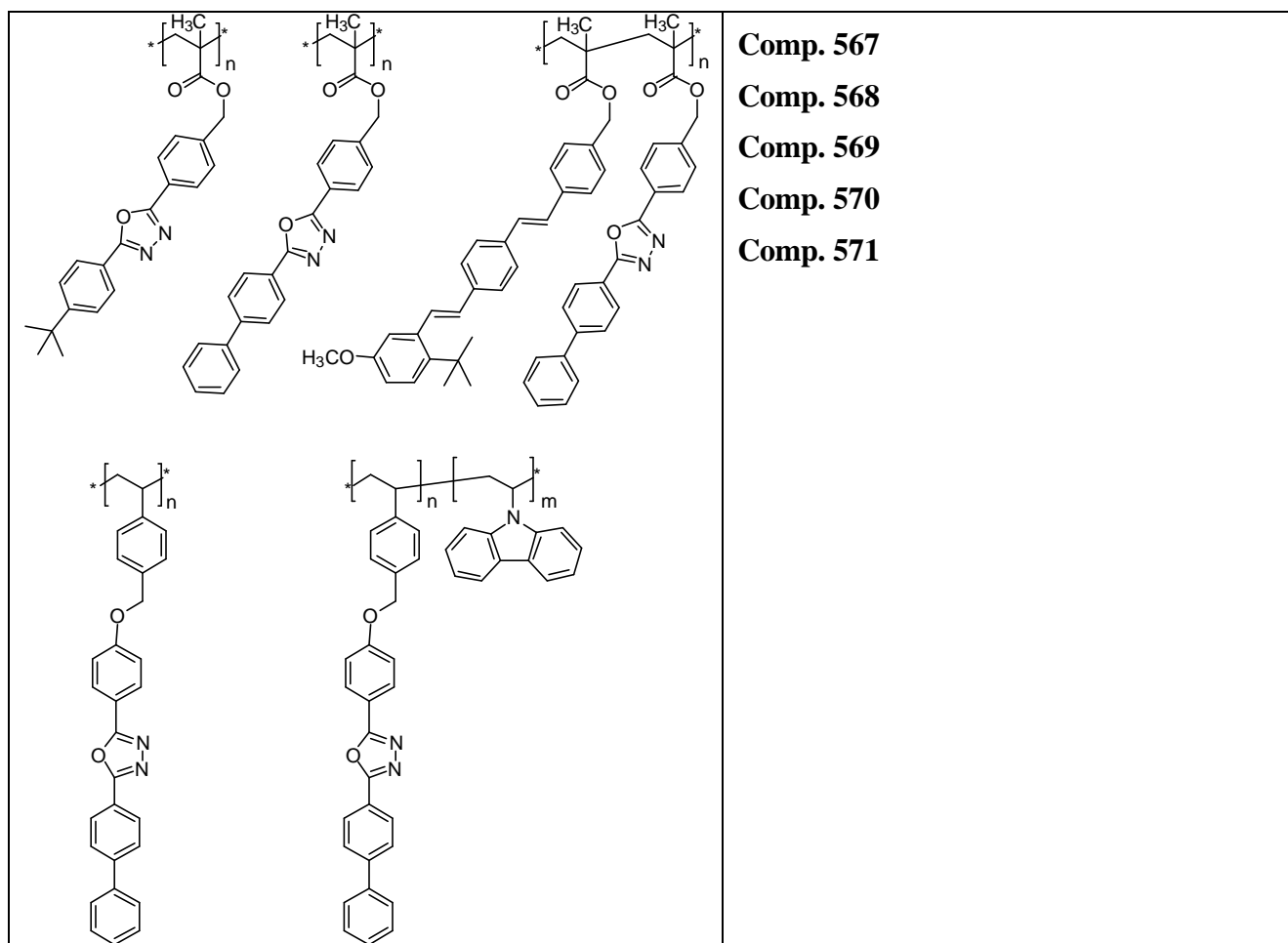


4.7. Oxadiazole and oxazole polymers.

The molecular materials based on oxadiazole heterocycle and, particularly, the PBD [2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole, (**Comp. 21**)] derivatives are among the most popular electron-transport materials for OLEDs, which is due to relatively high electron affinity and very good photoluminescence efficiency. The oxadiazole moieties, including the PBD, were introduced as pendant groups in many electroluminescent polymers in order to reduce the electron-injection barrier and improve the EL efficiency of the device. We have already described oxadiazole-containing PPVs

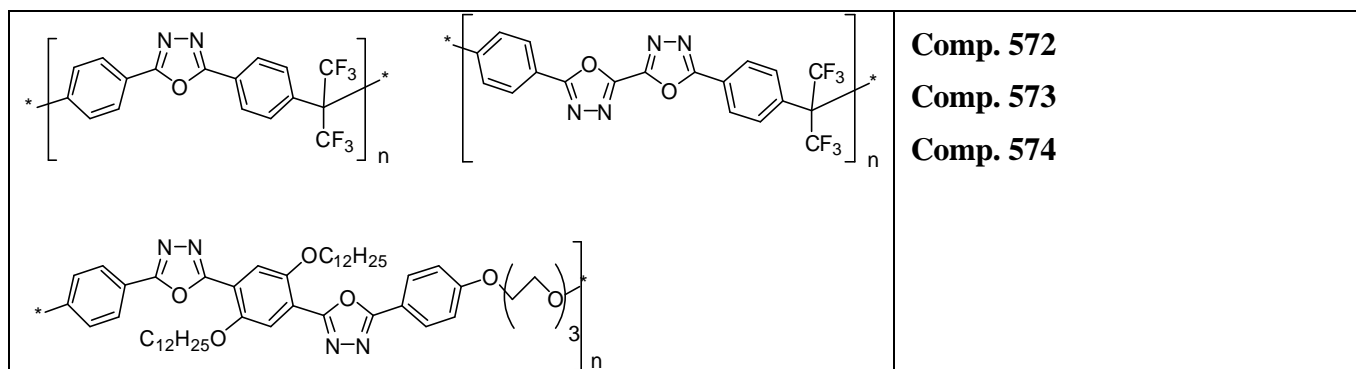
(**Comp. 61**, **Comp. 65–Comp. 68**), PFs (**Comp. 253**, **Comp. 254**, **Comp. 258–Comp. 261**) and PTs (**Comp. 452–Comp. 458**) in previous parts.

Blending the PBD with EL polymers have been employed in order to balance the charge injection/transport characteristics of the PLEDs.^{68,108,500,572} To avoid phase separation and molecular PBD crystallization several groups introduced the PBD moieties as pendant groups in non-conjugated polymetacrylate^{658,659,660} and polyethylene⁶⁵⁶ chains. Polymers **Comp. 567–Comp. 569** have been studied as materials for PLEDs,^{658,659} both in a single-layer devices and in combination with PPV hole-transporting layer. The authors mention that the device instability is a great problem for these systems, and engineering a more robust polymer backbone would be necessary. Later, Register et al. synthesized and studied related polymers **Comp. 570** and **Comp. 571** based on polystyrene backbone.⁶⁶¹ Observing the immiscibility of oxadiazole polymer **Comp. 570** with PVK, the authors designed the co-polymer **Comp. 571** containing both electron- and hole-transporting units. The device ITO/**Comp. 571**/Mg:Al showed improved external Q.E. of 0.3 %, although the turn-on voltage was still high (16 V). Doping the polymer with different molecular dyes, the emission color was tuned from blue to orange.⁶⁶¹



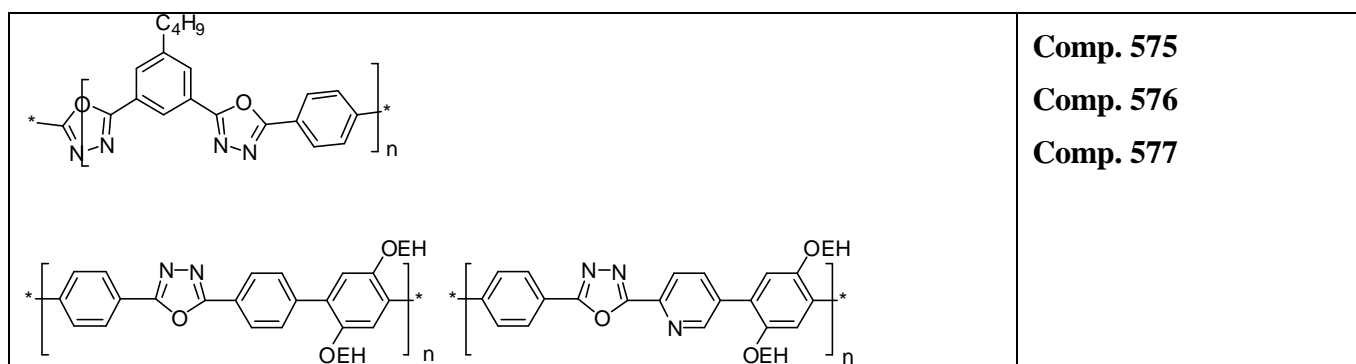
In 1995 Yang et al. reported polymers **Comp. 572**⁶⁶² and **Comp. 573**⁶⁶³ with a short conjugation length and wide π - π^* energy gap. They were not fluorescent but could be used as an electron-injection layer to significantly improve the Q.E. of PLEDs based on PPV electroluminescent material (from 0.002 % to 0.08 % for MEH-PPV **Comp. 13** and from 0.03 % to 0.30 % for BCHA-PPV **Comp. 23**).⁶⁶³ Additional oxadiazole moiety in **Comp. 573** further enhances the electron transport properties of the polymer and decreases the operation voltage of LEDs. Polymer **Comp. 574** with a

longer conjugation length has an efficient blue fluorescence ($\lambda_{\text{PL}} = 554, 465 \text{ nm}$, $\Phi_{\text{PL}}(\text{film}) = 35 \%$) and the PLED ITO/PANI/**Comp. 574**/**Comp. 572**/Ca emits a bright blue light with external Q.E. of 0.1 % (turn-on voltage 4.5 V).



Holmes et al. introduced oxadiazole moieties into formally conjugated (although having one meta-phenylene linkage) polymer **Comp. 575**.⁶⁶⁴ The polymerization was performed by condensation of terephthalaldihydrazide with 5-butyl-1,3-benzenedicarboxylic acid, followed by dehydration/cyclization of the formed polyhydrazide. Based on cyclic voltammetry studies, the authors concluded that an electron affinity of **Comp. 575**, although higher than that of MEH-PPV, is below that of, e.g., CN-PPVs, and only a moderate PL quantum yield (11%) was found.

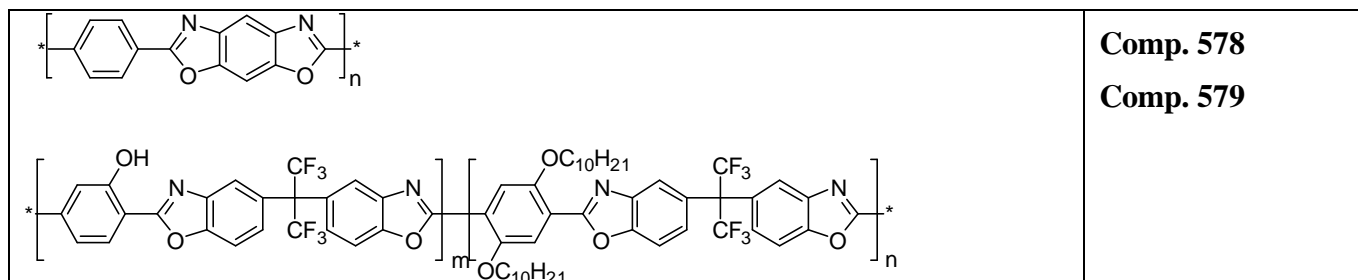
Inspired by good electron transport properties and high photoluminescence of PBD, and particularly, a claim by Heeger et al.⁶⁸ of exceptional performance of PBD/MEH-PPV mixture (EL of up to 50 % of the PL yield), Bryce et al. reported the first poly(PBD) homopolymer (**Comp. 576**) and its aza-derivative (**Comp. 577**).⁶⁶⁵ The device ITO/PEDOT/MEH-PPV:**Comp. 576**/Al showed external Q.E. yield of 0.26 %, as compared to 0.01 % obtained with MEH-PPV alone in an identically prepared device.



Several other oxadiazole and oxadiazole-containing polymers, which include fluorene moieties in the backbone have been prepared.

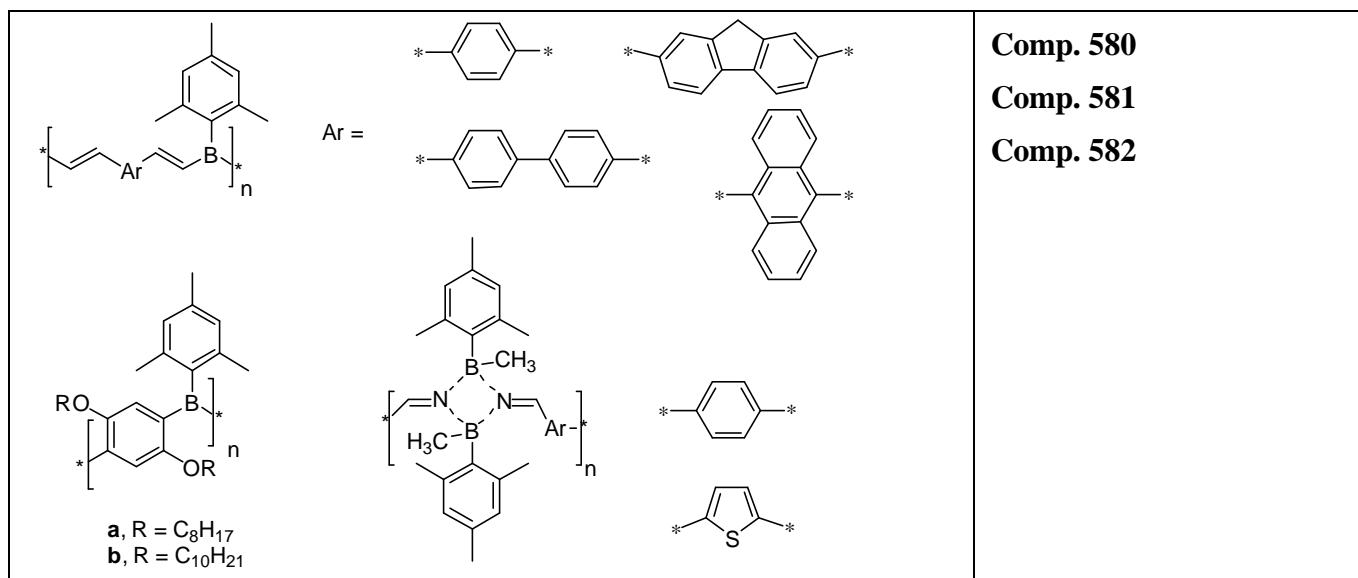
Very recently the studies in LEP were extended to benzoxazole-based polymers. The fully conjugated polymer **Comp. 578** was used in oriented fibers to create polarized PLEDs.⁶⁶⁶ The resulting

device ITO/**Comp. 578**/Al can be turned on at ~5 V emitting red light ($\lambda_{\text{EL}} = 620$ nm) with polarization ratio of 1.6. The same group reported EL from non-conjugated benzoxazole co-polymers **Comp. 579**.⁶⁶⁷ While the ratio $m:n$ decreases from 1:0 to 0:1 the emission band of **Comp. 579** broadens significantly (while keeping the maximum at ~520 nm), so that at $m:n = 0:1$ the emission band covers almost the entire visible region. The emission color of PLED fabricated as ITO/**Comp. 579**/Al can be tuned from green (CIE: $x = 0.25$, $y = 0.53$) to the color reported as white although the reported CIE coordinates ($x = 0.24$, $y = 0.30$) are relatively far from the definition of white (CIE: $x = 0.33$, $y = 0.33$).



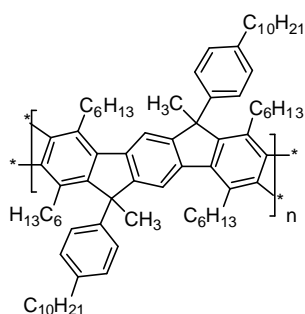
4.8. Boron-contained polymers.

Several relatively stable boron-contained conjugated polymers have been synthesized by Chujo et al. by high-yield hydroboration of $\text{C}\equiv\text{C}$ (for polymers **Comp. 580**⁶⁶⁸) or $\text{C}\equiv\text{N}$ (for polymers **Comp. 582**⁶⁶⁹) triple bonds or by Grignard-type reaction of phenylenedibromide with substituted dimethoxyborane in the presence of Mg (for polymers **Comp. 581**⁶⁷⁰). The conjugation in polymers is provided by interaction of π -system of organic units with vacant p-orbital of boron atom, which should greatly enhance the electron-transporting properties of the polymers. In solution **Comp. 580–Comp. 582** reveal strong blue or blue-green photoluminescence with $\lambda_{\text{PL}} = 440\text{--}496$ nm, although no electroluminescent devices have been reported so far, and the stability issue is likely to be a problem for practical applications of these materials.



4.9. Conclusions.

Although the major research activities in PLEDs are now concentrated in three major classes of LEPs – polyfluorenes, PPVs and, to a lesser extent, polythiophenes, the study of other classes of conjugated and nonconjugated polymers may give rise to high-performance EL materials with tunable emission color. Importantly, the charge-transport and charge-injection properties can be tuned in a wider region than it is accessible by structural modification of either of PF/PPV/PT materials. The very high EL performance achieved in PPP-type polymers (including ladder-PPPs) and very high chemical and thermal stability of the PPP materials render them as very promising candidates for commercial PLEDs. Based on LPPP **Comp. 524b** blue-green emitting PLEDs with external Q.E. up to 4%⁶⁰⁵ and the brightness as high as 40,000 cd/m²⁶⁷ was achieved by different engineering techniques. An efficient yellow-emitting PLED (external Q.E. of 4.2%⁵⁰⁵) and white emitting PLED (external Q.E. of 1.2%⁶¹¹) were fabricated by blending LPPP **Comp. 524b** with PT and PPE-based polymers, respectively.



Comp. 524b

LEP with heteroaromatic moieties (mainly with N and to a lesser extent with O and S heteroatoms) in the backbone of the polymer or as pendant group can substantially modify the LUMO level of the materials improving their electron transport properties and facilitating the electron injection in PLEDs but the efficiencies still lag behind the other systems.

5. Conclusions and Outlook.

In the previous four sections we have described the progress in the development of light-emitting polymers, from the beginning of 1990s till 2004. The practical application in polymer LEDs became a field of major research activities throughout the world, both in academia and in industrial labs. Over five hundred different LEPs described in this book (and, most probably, over a thousand reported LEPs) have been developed by common efforts of many researchers of different scientific background. On one hand, this fact is reflected in unsystematic and often illogical approaches the science took in the development of new materials (which was the biggest frustration for the authors who were trying to integrate all materials in one story). On the other hand, it allows an element of serendipity and keeps the scientific part of the field alive. Although at the moment the commercial success of PLEDs probably depends more on engineering issues, it would certainly not be possible without several important scientific breakthroughs. Besides the pioneering work of Friend et al on PPV-based PLEDs,¹ the following major discoveries should be listed (which is certainly not exhaustive):

- a) design of soluble light-emitting polymers by introduction of solubilizing substituents;
- b) prevention of interchain interactions (and resulting luminescence quenching) by sterically hindering substituents;
- c) fine tuning the emission of the polymers via copolymerization;
- d) control of the charge injection and transport by introduction of electron donor/acceptor substituents (or comonomers/end-capping groups);
- d) control of the interface at the anode and cathode;
- e) control of the film morphology as a function of spin-casting solvent.

Following these principles, a number of electroluminescent polymers, with external Q.E. of over 3–4%, have been demonstrated, although there are still a number of issues to solve for successful competition with small molecules OLEDs. Since one of the main targets for LEP is display technology; pure red, green and blue emitters are of particular importance. Among these, green color is the easiest to achieve. A very high performance of over 6% was demonstrated for a derivative of a traditional class of green-emitting polymers, phenyl-PPV **Comp. 88**,¹⁴⁰ as well as for a PF-based copolymer **Comp. 358**.⁴¹⁸ The photometric current efficiency of over 20 cd/A was demonstrated for these materials, which is also due to higher sensitivity of the human eye to green color. High efficiency red-emitting polymers are considerably less common, and, in terms of technology, this niche probably belongs to electrophosphorescent PLEDs (which are based on blends of conventional LEP with phosphorescent metal complexes, or their covalent conjugates; see [Chapter 7](#)). Speaking of the *electrofluorescence*, the best performing red emitters can be found among the fluorene copolymers with heterocyclic moieties, such as naphthoselenadiazole (**Comp. 342**: EL = 3.1%, 0.9 cd/A⁴¹¹). Design of a highly efficient polymer emitter giving a pure blue color is probably one of the major challenges to the LEP field. High energy excited states (~3 eV) generally impose higher reactivity (and lower stability) to blue emitters. Undoubtedly, polyfluorenes, as an easily functionalizable class of LEP, are the most promising materials for blue PLEDs. Although rather efficient (external Q.E. up to 3%) blue EL was also demonstrated by PPP polymers, the turn-on voltage (over 15–20 V) of the corresponding devices is much too high for display applications. Very pure blue color (CIE: x = 0.15, y = 0.08) is achieved for triarylamine-terminated dialkyl-PF **Comp. 223**.²⁴⁹ A photometric EL efficiency of 1.1 cd/A (turn-on voltage 3.5 V) was demonstrated for a corresponding single-layer PLED and this can be further pushed to 2–3 cd/A in multilayer device configurations.^{249,322} The color purity and color stability are the major concerns with blue-emitting polymers. A recent demonstration of keto-defect origin of the “parasitic” green band in PFs opens a number of possible (and already partially realized) solutions for this problem.

The next most promising application for electroluminescent polymers is general illumination, where high efficiency, stability and the low cost are the major criteria. Although the sufficiently high efficiency of yellow-emitting polymers (e.g., oxadiazole-containing PPV **Comp. 68**, photometric efficiency of 21.1 cd/A¹²⁴) are already available, the true need is in much less developed white-emitting LEPs. To date, true white color in LEP is available only by blending several types of materials. Thus, a pure white emission (CIE: $x = 0.31$, $y = 0.33$) was demonstrated by a blend of LPPP **Comp. 524b** with 1% of pyrene-containing PPE **Comp. 535**, although the achieved efficiency (1.2 cd/A) is still too low for practical applications.⁶¹¹

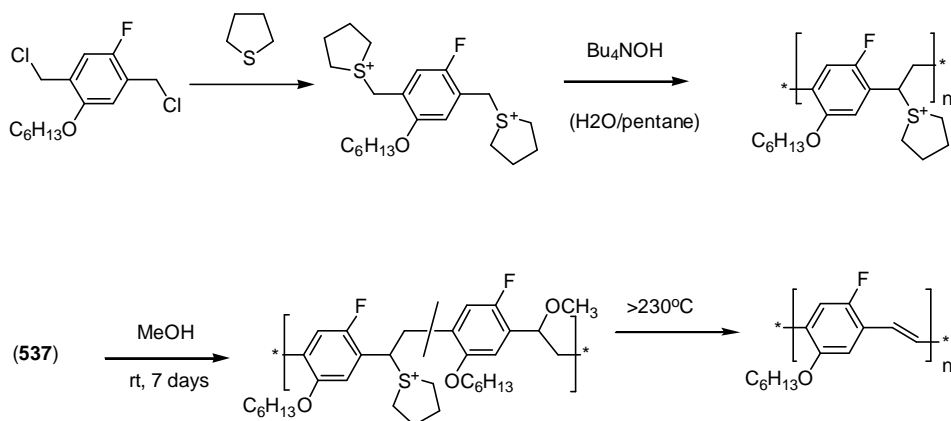
Overall, and for each one of the above examples, the stability, in terms of color and even more in terms of operation life-time, is the major issue for PLEDs. Current state-of-art operation half-life time of PLEDs rarely exceeds 10,000–20,000 h (which, in principle, could be acceptable for many applications), and even that is achievable for only few (mostly, green-emitting) polymers. A very significant role in the device degradation is played by material impurities, which are very difficult to control in polymers, as in any polydisperse system. Rigorous monomer purification and a careful choice of the polymerization method are just as-important for the EL performance as the specific polymer structure. At the same time, the device architecture is also directly responsible for the device efficiency and stability. A careful adjustment of charge injection barriers can minimize the driving voltage and improve the device efficiency and stability. To conclude, the future progress in polymer LED will depend on a close collaboration between organic and polymer chemists on one side, and surface scientists and engineers on the other.

6. Appendix.

6.1. Synthesis of poly(p-phenylene vinylene)s

6.1.1 The Wessling-Zimmerman (thermoconversion) precursor route to PPV

Poly(2-fluoro-5-(*n*-hexyloxy)-1,4-phenylene vinylene) **Comp. 77**.



Comp. 583

Comp. 584

Comp. 585

Comp. 586

[From Ref. 130, © American Chemical Society].

Bis(tetrahydrothiophenium) salt **Comp. 584.** Bis(chloromethyl)benzene **Comp. 583** (1.22 g, 3.19 mmol) was suspended in a solution of tetrahydrothiophene (1.4 g, 15.9 mmol) in 35 mL of dry methanol. The mixture was stirred at 55°C for 24 h. The solvent and excess tetrahydrothiophene were removed by distillation to give an off-white residue which was dissolved in a minimum amount of methanol and precipitated into 200 mL of dry acetone. After vacuum drying, white powder **Comp. 584** (1.25 g, 70%) was obtained with mp $163\text{--}166^\circ\text{C}$ (dec). This compound is stable in a freezer under inert atmosphere. An analytical sample was obtained by 3-fold precipitation from methanol into acetone. Anal. Calcd. for $\text{C}_{22}\text{H}_{35}\text{Br}_2\text{FOS}_2$: C, 47.32; H, 6.31; Br, 28.62; F, 3.40, S, 11.48. Found: C, 47.38; H, 6.27; Br, 29.1; F, 3.50; S, 11.52. ^1H NMR (80 MHz, CD_3OD): 7.64 (d, 1 H, $J = 8.8$ Hz), 7.52 (d, 1 H, $J = 4.5$ Hz), 4.77 (s, 2 H), 4.67 (s, 2 H), 4.29 (t, 2 H, $J = 6.2$ Hz), 3.66 (m, 8 H), 2.48 (m, 8 H), 1.54 (m, 8 H), 1.02 (asym t, 3 H, $J = 7.5$ Hz).

Polyelectrolyte **Comp. 585.** The bis(sulfonium) salt **Comp. 584** (600 mg, 1.08 mmol) was dissolved in 25 mL of distilled water. The solution was filtered through a glass frit and placed in a 100 mL round-bottom flask. An equal volume of pentane was added to the flask, and the two-phase system was cooled to 0°C under argon. A solution of tetramethylammonium hydroxide was also cooled to 0°C under argon/pentane. Both solutions were thoroughly purged with argon gas for 1 h. Then, the base (0.47 mL, 1.30 mmol) was added swiftly by syringe. The polymerization was allowed to proceed for 1 h at 0°C . The excess base was neutralized with 6 M HCl solution to a phenolphthalein end point. The resulting yellow-green solution was dialyzed against distilled water (Spectropore 1 filters, M_w cutoff 6,000–8,000) for 3 days to give a uniform green solution. This solution can be used to cast films which are

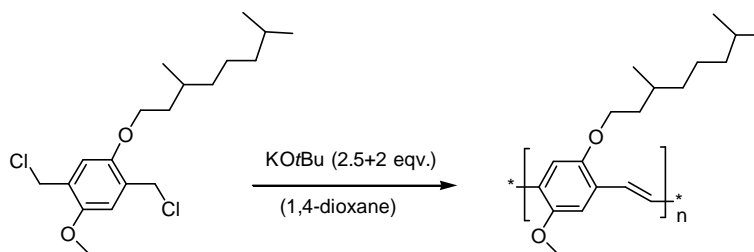
soluble in methanol but insoluble in THF and CHCl_3 . This material is appropriate for conversion to polyether **Comp. 586**.

Polyether Comp. 586. The sulfonium polyelectrolyte **Comp. 585** was dissolved in a minimal amount of methanol. The solution was stirred for 1 week under argon, during which pendant polyether **Comp. 586** precipitated from the solution. The tacky yellow material was completely soluble in CHCl_3 and THF. **Comp. 586** can be dissolved in THF and passed through a 0.2 mm filter for gel permeation chromatography or for use in film casting and device fabrication. Cast films can be completely redissolved into CHCl_3 or THF. Gel permeation chromatography in tetrahydrofuran (polystyrene standards) gave $M_w = 91,500$ and $M_n = 33,800$.

PPV Comp. 77. A film of polyether **Comp. 586** was clamped between two 0.125 in-thick Teflon plates, and then heated at $230\text{ }^\circ\text{C}$ for 6 h under vacuum ($<0.01\text{ mmHg}$) to give a red film of PPV **Comp. 77**. The final polymer films are insoluble in CHCl_3 , THF, and MeOH. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{OF}$: C, 76.33; H, 7.78; F, 8.62; S, 0.0. Found: C, 72.02; H, 7.44; F, 8.3; S, 0.30. IR (neat film, cm^{-1}): 962 (*trans* HC=CH). UV-vis (neat film on quartz): $\lambda_{\text{max}} = 455\text{ nm}$. PL (neat film on quartz, excitation at 390 nm): $\lambda_{\text{max}} = 630\text{ nm}$.

6.1.2 Gilch polymerization procedure.

Preparation of Poly[2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-phenylenevinylene] **Comp. 14**.



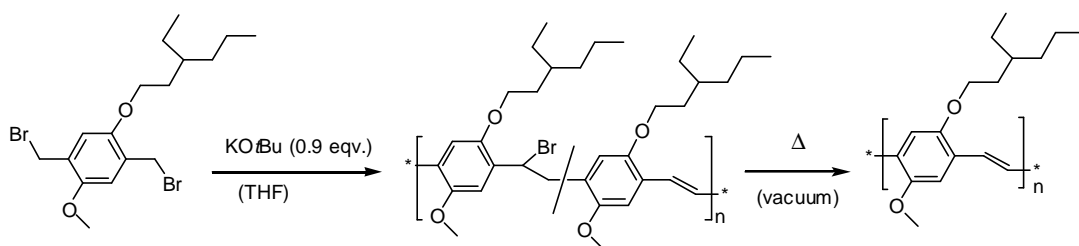
[From Ref. 38, © American Chemical Society].

A 4 L four-neck flask fitted with mechanical (Teflon) stirrer, reflux condenser, thermometer, and dropping funnel was dried (stream of hot air) and flushed with N_2 . The reactor was then charged with 2.3 l of dry 1,4-dioxane, and the solvent was degassed by passing N_2 through it for about 15 min. The solvent was heated to $98\text{ }^\circ\text{C}$ with an oil bath, and 14.0 g (38.7 mmol) of 2,5-bis(chloromethyl)-1-(3,7-dimethyloctyloxy)-4-methoxybenzene was added as a solid. (The solid was rinsed in with about 10 mL of dry 1,4-dioxane.) A 11.3 g (100 mmol, 2.6 equiv) sample of potassium *tert*-butoxide, dissolved in 100 mL of 1,4-dioxane, was added dropwise to the reaction solution from the dropping funnel over a period of 5 min. During this addition, the reaction mixture changed color from colorless via greenish to yellow/orange, and the viscosity increased significantly. After the addition was complete, the mixture was stirred further for about 5 min at $98\text{ }^\circ\text{C}$; 8.70 g of potassium *tert*-butoxide (77 mmol, 2 equiv) in 77 mL of dry 1,4-dioxane was then added over a period of 1 min, and stirring was continued for 2 h at $96\text{--}98\text{ }^\circ\text{C}$. The solution was then cooled to $50\text{ }^\circ\text{C}$ over a period of about 2 h. The reaction mixture was finally mixed with 15 mL (260 mmol, 1.5 equiv based on the base) of acetic acid (diluted with the same amount of 1,4-dioxane) and stirred further for 20 min. The solution was then deep orange and the viscosity increased. For the workup, the reaction solution was slowly poured into 2.5 L of intensively stirred water. The resulting mixture was stirred further for 10 min, 200 mL of methanol was added, and the precipitated polymer was filtered off. This was washed with 200 mL of methanol and dried under reduced pressure at room temperature. A 10.04 g (34.8 mmol, 90%) sample of crude polymer was obtained as red fibers. The polymer was purified by dissolving it in 1.1 L of THF ($60\text{ }^\circ\text{C}$), cooling the

solution to 40 °C, and precipitating the polymer by dropwise addition of 1.2 L of methanol. After washing with 200 mL of methanol, it was dried at room temperature under reduced pressure. This procedure was repeated once more using 1.0 L of THF/1.0 L of methanol. A 6.03 g (20.9 mmol, 54%) sample of poly[2-(3,7-dimethyloctyloxy)-5-methoxy-*p*-phenylenevinylene] (**Comp. 14**) was obtained as a dark orange, fibrous polymer. ¹H NMR (400 MHz, CDCl₃): 7.7–6.5 (br m, 4 H; H_{arom}, olefin-H); 4.5–3.6 (br m, 5 H; OCH₃, OCH₂); 2.1–0.6 (br m, 19 H; aliph-H). GPC (THF + 0.25% of oxalic acid; column set SDV500, SDV1000, SDV10000 (from PSS), 35 °C, UV detection at 254 nm, polystyrene standard): $M_w = 1.5 \times 10^6$ g/mol, $M_n = 3.1 \times 10^5$ g/mol. Elemental analysis: calc.: C, 79.12%; H, 9.78%; O, 11.09%. Found: C, 78.88%; H, 9.82%; O, 11.00%; Cl, 25 ppm; K, 41 ppm; Na, 23 ppm.

6.1.3 Chlorine (bromine) precursor route (CPR)

Preparation of Poly { 2-[2'-ethylhexyloxy]-5-[4''-methylsulfonylphenyl]-1,4-phenylenevinylene } (**Comp. 70**).



Comp. 587

[From Ref. 126, © American Chemical Society].

A solution of potassium *tert*-butoxide dissolved in dry tetrahydrofuran (0.3 M, 2.6 mL, 0.8 mmol) was added to a solution of bis(bromomethyl)methylsulfonylbiphenyl (0.5 g, 0.9 mmol) in dry tetrahydrofuran (3 mL) cooled in an acetone/ice bath under nitrogen. A bright yellow viscous solution was formed, and dry tetrahydrofuran (4 mL) was added. The reaction mixture was allowed to warm to room temperature after 10 min and stirred for 2 h. A small amount of a precipitate was formed. The reaction mixture was filtered through a plug of cotton wool, and the polymer **Comp. 587** was precipitated by adding the reaction mixture dropwise to icecold 2-propanol (50 mL). The mixture was centrifuged for 10 min at 4000 rpm, and the supernatant was removed. The crude polymer **Comp. 587** was briefly dried under vacuum, dissolved in dry tetrahydrofuran, and then precipitated by addition to an excess of 2-propanol. The solid was collected after centrifugation, and the process was repeated a further two times. The residue was finally collected by dissolution in a minimum of tetrahydrofuran, and the solvent was removed to leave **Comp. 587** as an orange/yellow solid (200 mg, 40%).

Characterization: λ_{\max} (thin film)/cm⁻¹ 955 (HC=C), 1154 (SO₂), 1315 (SO₂); λ_{\max} (CH₂Cl₂)/nm 300sh; ¹H NMR (500 MHz: CDCl₃) 0.74–1.00 (br m, CH₃), 1.14–1.90 (br m, CH and CH₂), 2.94–3.25, 3.30–4.10 (br m, CH₃SO₂, OCH₂, and ArCH₂), 5.05–5.23 (br s, CHBr), 6.27–7.63 (br m, ArH or vinyl H), 7.67–8.05 (br m, ArH); gel permeation chromatography of equilibrated sample, $M_w = 2.7 \times 10^5$ and $M_n = 1.3 \times 10^5$, PDI = 2.1.

Thin films of **Comp. 587** were heated at 160 °C under a dynamic vacuum for 14 h to yield **Comp. 70**. Characterization: λ_{\max} (film on KBr disk)/cm⁻¹ 955 (C=CH), 1154 (SO₂), 1315 (SO₂); λ_{\max} (thin film)/nm 285sh, 437.

6.1.4 Heck coupling route

Preparation of Poly[2,5,2',5''-tetraoctyl-*p*-terphenyl-4,4'-ylenevinylene-*p*-phenylenevinylene] (Comp. 91).



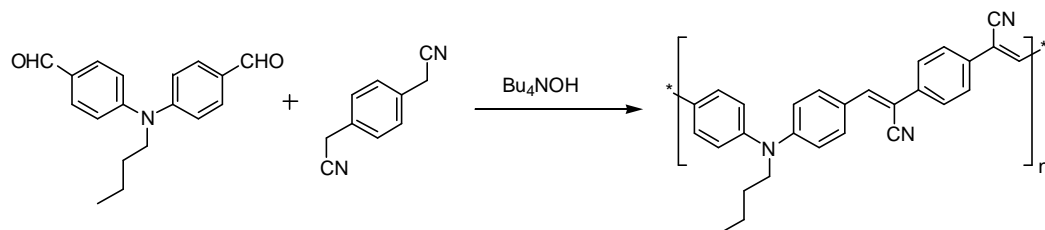
Comp. 588

[From Ref. 46, © American Chemical Society].

A mixture of monomer **Comp. 588** (1.0 g 1.2 mmol), *p*-divinylbenzene (0.155 g, 1.2 mmol), $\text{Pd}(\text{OAc})_2$ (0.011 g, 0.05 mmol), tri-*o*-tolylphosphine (0.071 g, 0.23 mmol), triethylamine (2 mL), and DMF (5 mL) was placed in a heavy-wall pressure tube. The tube was degassed, closed (Teflon bushing), and heated to 100 °C. After 40 h of reaction, thin-layer chromatography showed that the monomers were consumed. The reaction mixture was then poured into methanol (75 mL). The precipitated material was filtered off and dried under vacuum, giving a brown-yellow polymer (0.88 g, conversion = 91%). The crude polymer was dissolved in chloroform and then filtered through a small column of Kieselgel to remove traces of catalyst. The resulting solution was concentrated and precipitated in methanol (75 mL). The yellow polymer was collected by filtration and thoroughly dried under vacuum. ^1H NMR (broad signals): 0.89 (t, CH_3 , 12H), 1.25/1.29/1.5 (m, CH_2 , 48H), 2.64 (m, CH_2 , 8H), 7.1–7.6 (3 main peaks, arom CH and vinyl CH, 16H); ^{13}C NMR: 126.8, 128.8, 129.2, 130.1, 131.5 (arom CH), 134.7, 137.2, 137.6, 138.1, 138.2, 140.1 (arom C). Anal. Calcd for $\text{C}_{60}\text{H}_{84}$ (repeating unit): C, 89.49; H, 10.51. Found: C, 88.02; H, 10.51; Br, 0.89.

6.1.5 Knoevenagel coupling route

Preparation of CN-PPV co-polymer (Comp. 120).



Comp. 589

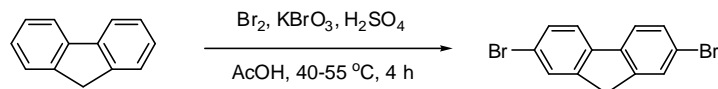
[From Ref. 155, © American Chemical Society].

Under an argon atmosphere, to a stirred solution of equimolar quantities of dialdehyde **Comp. 589** and 1,4-phenylenediacetonitrile in tetrahydrofuran and *tert*-butyl alcohol (1:1) was added dropwise 5 mol% of Bu_4NOH (1M in methanol) at 45 °C for 20 min. The resulting paste-like polymeric product that precipitated from the solution during polymerization was collected and thoroughly washed with methanol to remove ionic species and unreacted compounds. The scarlet polymeric product was dried in a vacuum oven at 40 °C for 2 days. The polymer yield was 93%. GPC (THF, polystyrene standard): $M_w = 1.5 \times 10^6$ g/mol, $M_n = 3.1 \times 10^5$ g/mol

6.2. Synthesis of polyfluorenes

6.2.1. Synthesis of PF monomers.

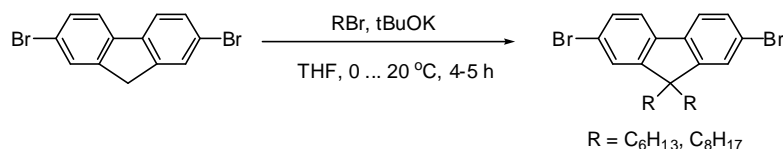
2,7-Dibromofluorene.



Comp. 590

Fluorene (292 g, 1.76 mol) was dissolved in acetic acid (2.6 L) at $\sim 70\text{ }^\circ\text{C}$ and H_2SO_4 (96%, 25 mL) was added slowly to this solution. The reaction mixture was allowed to cool to $\sim 50\text{ }^\circ\text{C}$ with stirring, and a solution of bromine (150 mL, 2.92 mol) in acetic acid (200 mL) was added dropwise for 2–3 h, keeping the temperature at $40-55\text{ }^\circ\text{C}$ to avoid crystallization of the fluorene. When ca. $1/3 - 1/2$ of bromine was added, dibromofluorene started to crystallize. Simultaneously with addition of a second half of bromine, KBrO_3 (100 g, 0.60 mol) was added in small portions (CAUTION: add slowly, exothermic reaction !) at $40-55\text{ }^\circ\text{C}$ with intense stirring, which promotes intensive precipitation of dibromofluorene. The mixture was stirred for 3–4 h allowing to cool gradually to room temperature. After cooling the mixture to $10\text{ }^\circ\text{C}$, the solid was filtered off, washed with 70% AcOH (0.5 L) and water until pH 7, and dried affording crude product as creme-colored solid (481 g, 85 %) of $> 95\%$ purity (by ^1H NMR). To further purify the product it was stirred in AcOH ($\sim 1\text{ L}$) at reflux (no full dissolution) for 4 h, cooled, filtered off, washed with AcOH and dried (455 g, 80%).

2,7-dibromo-9,9-dihexylfluorene (adapted from ref. 298).



Comp. 590

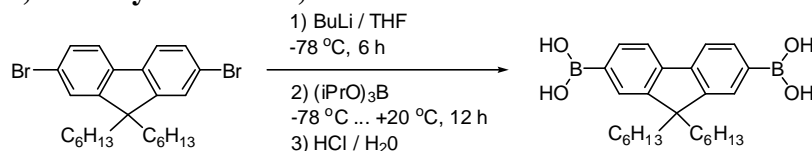
Comp. 591

Comp. 592

Under argon, 3 L three-neck flask was charged with 2,7-dibromofluorene (130.0 g, 0.40 mol), 1-bromohexane (220 mL, 1.57 mol) and dry THF (1.0 L). After the full dissolution the mixture was cooled to $0\text{ }^\circ\text{C}$ and a solution of potassium *tert*-butoxide (100.6 g, 0.90 mol) in dry THF (1.0 L) was added dropwise at $0 - +5\text{ }^\circ\text{C}$ with vigorous stirring during 1.5 h. Upon adding the *tert*-butoxide solution the reaction mixture become orange (generation of fluorene anion) and then the color vanished to light pink (at the end of *tert*-butoxide addition no orange color is produced). The mixture was stirred at room temperature for 4 h, filtered off from the KBr precipitate, and the solid was washed on a filter with DCM. The filtrate was evaporated on rotavapor, the residue was dissolved in DCM (1.5 L), washed with water, dried over MgSO_4 , and the solvent was evaporated. Excess of 1-bromohexane was removed *in vacuo* ($80\text{ }^\circ\text{C}$, 1 mbar) yielding crude product (196.7 g, 99.6 %) as yellow crystals. This was purified by column chromatography ($7 \times 17\text{ cm}$ column, silica gel, eluent – petrol ether bp $40-60\text{ }^\circ\text{C}$) to afford 2,7-dibromo-9,9-dihexylfluorene **Comp. 591** (179.5 g, 90.9 %) as colorless plates. The material can also be additionally recrystallized from hexane or ethanol.

2,7-dibromo-9,9-dioctylfluorene Comp. 592 was obtained as described above procedure and after the column chromatography was additionally recrystallized from ethanol yielding pure product in 78% yield.

9,9-dihexylfluorene-2,7-diboronic acid.

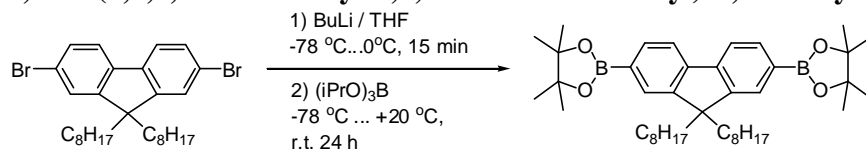


Comp. 591

Comp. 593

To a stirred solution of 2,7-dibromo-9,9-dihexylfluorene (30.0 g, 60.9 mmol) in dry THF (1.0 L) under argon, solution of BuLi in hexane (2.5 M; 54 mL, 135 mmol) was added dropwise at $-78\text{ }^{\circ}\text{C}$. The mixture was stirred at this temperature for 6 h to give a white suspension. Triisopropylborate (60 mL, 258 mmol) was added quickly and the mixture was stirred overnight allowing the temperature rise gradually to r.t. Water (300 mL) was added and the mixture was stirred at r.t. for 4 h. Organic solvents were removed on rotavapor ($35\text{ }^{\circ}\text{C}$, 40 mbar), water (1.1 L) was added and the mixture was acidified with concentrated HCl. The product was extracted into diethyl ether ($7 \times 300\text{ mL}$), organic layer was dried over MgSO_4 and solvent was removed on rotavapor. The residue was dissolved in acetone (110 mL) and reprecipitated into mixture of water (130 mL) and concentrated HCl (70 mL) affording desired product (24.3 g, 94.5 %) as white powder. The product can be additionally purified by dissolution in acetone (100 mL) and addition of hexane (200 mL) to this solution.

2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene.



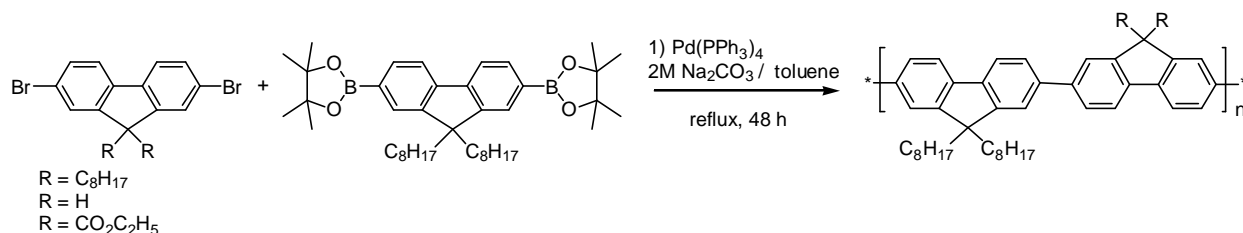
Comp. 592

Comp. 594

[From Ref. 384. © 2004 American Chemical Society].

To a stirred solution of 2,7 dibromo-9,9-dioctylfluorene (5.0 g, 9.1 mmol) in THF (70 mL) at $-78\text{ }^{\circ}\text{C}$ was added dropwise *n*-butyllithium in hexanes (7.6 mL, 2.5 M, 19 mmol) at $-78\text{ }^{\circ}\text{C}$. The mixture was warmed to $0\text{ }^{\circ}\text{C}$ for 15 min and then cooled back to $-78\text{ }^{\circ}\text{C}$. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4.0 g, 21.5 mmol) was added rapidly to the solution, and the resulting mixture was warmed to room temperature and stirred for 24 h. The mixture was then poured into water and extracted with diethyl ether. The organic extract was washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by column chromatography eluting with 2% ethyl acetate/hexane to give 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene as a pale yellow solid (3.80 g, 65%). HRMS: Calcd for $\text{C}_{41}\text{H}_{64}\text{B}_2\text{O}_4$: 642.59. Found: 642.37. ^1H NMR (250 MHz CD_2Cl_2): δ 7.83 (d, 2H), 7.76 (s, 2H), 7.73 (d, 2H), 2.05 (m, 4H), 1.44 (s, 24H), 1.25–1.09 (m, 20 H), 0.82 (t, 6H), 0.59 (m, 4H). ^{13}C NMR (62.5 MHz, CD_2Cl_2): δ 150.35, 143.82, 133.84, 128.74, 119.23, 83.51, 54.96, 39.36, 31.68, 29.89, 29.08, 29.00, 24.87, 23.50, 22.49, 13.96.

6.2.2. Suzuki coupling polymerization.



[From Ref. 279 © 1997 American Chemical Society].

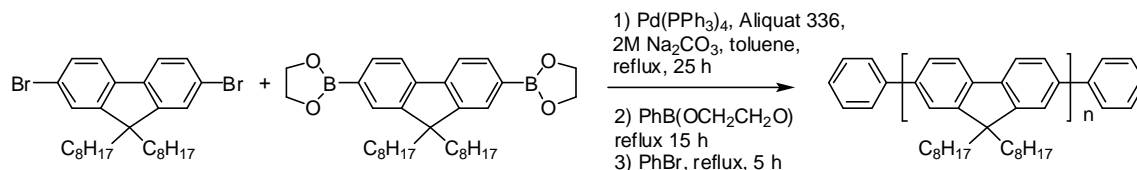
Carefully purified 2,7-dibromofluorene derivative (1 equiv), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene Comp. 594 (1 equiv), and $Pd(PPh_3)_4$ (1.5–0.5 mol %) were dissolved in a mixture of toluene ([monomer] = 0.5 M) and aqueous 2 M Na_2CO_3 (or K_2CO_3) (1:1.5 toluene). The solution was first put under a nitrogen atmosphere and was refluxed with vigorous stirring for 48 h. The whole mixture was then poured into methanol (150 mL). The precipitated material was recovered by filtration through a Büchner funnel and washed with dilute HCl. The solid material was washed for 24 h in a Soxhlet apparatus using acetone to remove oligomers and catalyst residues. The resulting polymers were soluble in THF and $CHCl_3$. Yields: ~65–90 %.

Poly[2,7-(9,9-dioctylfluorene)] Comp. 188. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.85 (2H, d), 7.68 (4H, m), 2.15 (4H, m), 1.2 (24H, m), 0.8 (6H, t).

Poly[2,7'-(9,9-dioctyl-2',7-bifluorene)]. 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.1–8.0 (12H, m), 4.0 (2H, s), 2.1 (4H, m), 1.1 (24H, m), 0.8 (6H, t).

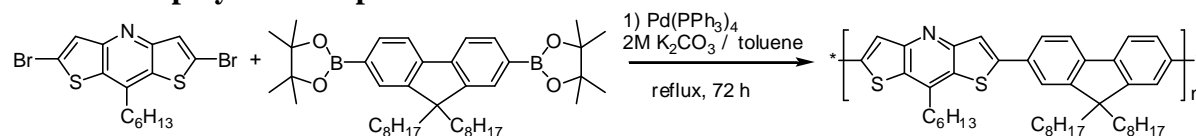
Poly-2,7'-(diethyl 9,9-dioctyl-2,7'-bifluorene-9',9'-dicarboxylate). 1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.2 (2H, s), 7.75 (5H, m), 7.65 (5H, m), 4.45–4.2 (4H, m), 2.1 (4H, m), 1.7 (1.5H, m), 1.4–1.0 (24H, m), 0.9–0.6 (6H, 2t).

Suzuki polymerization in presence of phase transfer catalyst: Poly(9,9-dioctylfluorene) Comp. 188.



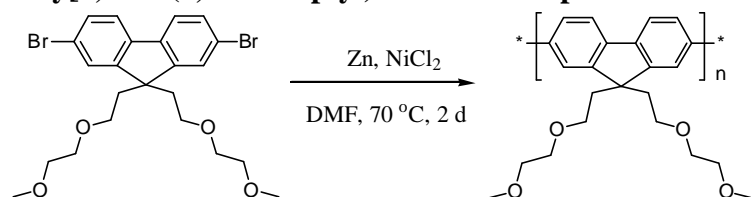
[From ref. 280, US Patent 5,777,070, Jul. 7, 1998]. {must be substituted with a method from a journal; copyright from patents is not easy}

To a mixture of 9,9-dioctylfluorene-2,7-di(ethyleneboronate) (15.8 g, 29.49 mmol), 2,7-dibromo-9,9-dioctylfluorene (16.18 g, 29.49 mmol) in toluene (130 mL) under nitrogen is added Aliquat[®] 336 (1.5 g, 3.7 mmol), $Pd(PPh_3)_4$ (0.18 g, 0.15 mmol), and 2M aqueous sodium carbonate (50 mL, 100 mmol). The mixture is stirred vigorously and heated at gentle reflux for 2 hours when a viscous reaction mixture is observed. An additional 50 mL of toluene is added and the reaction continued for another 15 hours. 60 mL of toluene is then added to the very viscous mixture and the heating and stirring are continued for 9 more hours. At the end of this period, the polymer is capped by adding 2 g of phenyl ethyleneboronate followed by heating for 15 hours, and 1 g of bromobenzene followed by heating for 5 hours. The reaction mixture is cooled to about 60 °C and is added slowly to a stirred solution of 3 L of methanol and 300 mL of deionized water. The fibrous polymer is collected by filtration and is washed successively with methanol (500 mL), deionized water (200 mL), and methanol (800 mL), and the dried *in vacuo* at 60 °C for 10 hours. The polymer weighed 23 g (100 % yield). The inherent viscosity of the polymer is 1.50 dL/g. $M_w = 148,000$ g/mol, $M_n = 47,980$ g/mol (GPC, against polystyrene standard).

Fluorene copolymer Comp. 302.**Comp. 595****Comp. 594****Comp. 302**

[From Ref. 384. © 2004 American Chemical Society].

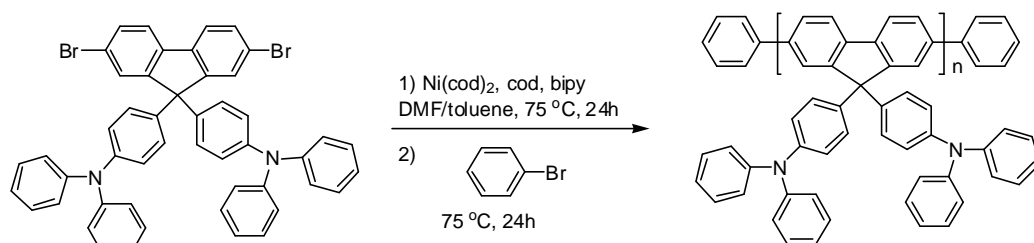
A solution of 2,6-Dibromo-4-hexylbithieno[3,2-*b*:2'3'-*e*]pyridine Comp. 595 (0.300 g, 0.466 mmol), 9,9-dioctylfluorene-2,7-di(ethyleneboronate) Comp. 594 (0.202 g, 0.466 mmol), and Pd(PPh₃)₄ (0.020 g, 0.5 mol %) in a mixture of toluene (15 mL) and aqueous 2 M K₂CO₃ (10 mL) was refluxed with vigorous stirring for 72 h under N₂. The cooled mixture was poured into methanol (150 mL), and the precipitate was recovered by filtration and washed with dilute HCl. The precipitate was then extracted with acetone in a Soxhlet apparatus for 24 h. The dried residue was dissolved in dichloromethane and stirred with EDTA solution overnight. The residue of crude polymer was twice dissolved in chloroform and reprecipitated from methanol to give the copolymer **Comp. 302** as a yellow solid (0.2 g, 67%). Elemental analysis: Found: C 79.09, H 3.15, N 2.11, S 5.23%. Calculated: C 79.58; H 8.65, N 2.11, S 9.66%. GPC: M_n = 10 577 g/mol, M_w = 31 297 g/mol, PDI = 2.95. ¹H NMR (250 MHz, CD₂Cl₂): δ 7.88 (s, 2H), 7.82 (m, 2H), 7.59 (m, 2H), 7.24 (d, 2H) 3.10 (t, 2H) 2.1 (m, 6H), 0.9 (m, 40 H). ¹³C NMR (62.5 MHz, CD₂Cl₂): δ 155.54, 152.60, 142.00, 141.86, 138.89, 128.40, 121.17, 120.99, 120.67, 40.58, 34.64, 32.13, 31.93, 30.29, 29.54, 25.11, 22.95, 14.18.

6.2.3. Yamamoto polymerization.**Poly[9,9-bis(3,6-oxaheptyl)fluorene Comp. 190.**

[From Ref. 270. US Patent 5,900,327, May 4, 1999]. {must be substituted with a method from a journal or removed; copyright from patents is not easy}

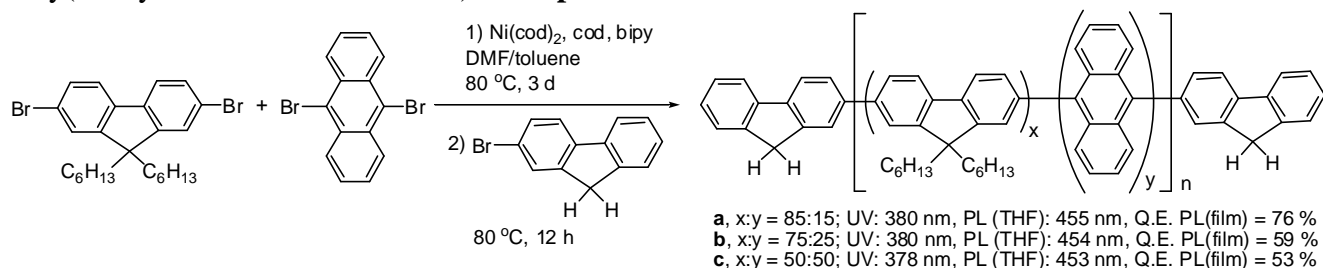
9,9-bis(oxaheptyl)-2,7-dibromofluorene (5.0 g), triphenylphosphine (2.59 g), zinc dust (3.94 g), 2,2'-dipyridyl (0.13 g), and nickel chloride (0.11 g) were placed in a 100 mL flask and purged with nitrogen. N,N-Dimethylformamide (40 mL) was added via syringe and the mixture was stirred at 70 °C for 2 days. The mixture was cooled, filtered and dialyzed (MWCO = 1,000) against methanol and water. The solid that precipitated was collected on filter paper and redissolved in THF. The solution was poured into water to effect precipitation of light yellow solid which was further purified by dissolution in THF and precipitation in methanol. 0.74 g (21 %) of light yellow solid was obtained. M_w = 214,900 g/mol, M_n = 94,200 g/mol (GPC, against polystyrene standard); UV: 380 nm, PL: 432, 450, 540 nm, Φ_{PL} = 78 % (films).

Poly[9,9-bis(4-diphenylaminophenyl)-2,7-fluorene] Comp. 217.

**Comp. 596**

[From Ref. 318 © 2002 Wiley-VCH].

A solution of $\text{Ni}(\text{cod})_2$ (132 mg, 0.48 mmol), 2,2'-bipyridine (75 mg, 0.48 mmol) and 1,5-cyclooctadienyl (52 mg, 0.48 mmol) in dry DMF (3 mL) was heated at 75 °C for 30 min under an argon atmosphere. A solution of the monomer **Comp. 596** (355 mg, 0.44 mmol) in dry toluene (5 mL) was added and the mixture was heated at 75 °C for a further 24 h and then poured into a methanol/HCl (2:1) mixture. The crude product was collected, dissolved in CHCl_3 and then precipitated from methanol/acetone (4:1). Residual impurities were removed by extraction with acetone in a Soxhlet apparatus to give polymer **Comp. 217** (277 mg, 97%). GPC (THF) M_n : 12,060 g/mol, M_w : 25,240 g/mol, PDI 2.1 (polystyrene standards)/ ^1H -NMR (300 MHz, $\text{C}_2\text{D}_2\text{Cl}_2$): 6.60-6.72 (m, 28H, aryl H), 7.40-7.69 (b, 4H, fluorenyl H), 7.70-7.96 (b, 2H, fluorenyl H). ^{13}C -NMR (126MHz, $\text{C}_2\text{D}_2\text{Cl}_2$): 64.6, 120.6, 123.1, 123.3, 124.7, 125.3, 129.1, 129.4, 139.7, 146.6, 146.9, 148.0, 152.8. λ_{max} (CHCl_3): 308, 384 nm. PL (CHCl_3) 441, 419 nm; (film) 428, 452 nm.

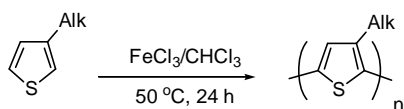
Poly(dialkylfluorene-co-anthracene)s **Comp. 235a-c**:

[From Ref. 333, © 1998 Wiley-VCH].

Into a Schlenk tube was placed bis(1,5-cyclooctadiene)-nickel(0) (2.6 mmol), 2,2'-bipyridyl (2.6 mmol), 1,5-cyclooctadiene (0.2 mL), DMF (4 mL), and toluene (8 mL). The reaction mixture was heated to 80 °C for 0.5 h under argon. The dibromide comonomers dissolved in degassed toluene (8 mL; molar ratio of dibromides to nickel complex: 0.65) were added under argon to the DMF/toluene solution and the polymerization maintained at 80 °C for 3 days in the dark. 2-Bromofluorene (molar ratio of dibromides to monobromide: 0.1) dissolved in degassed toluene (1 mL) was added and the reaction continued for 12 h. The polymers were precipitated by addition of the hot solution dropwise to an equivolume mixture of concentrated HCl, methanol, and acetone. The isolated polymers were then dissolved in toluene or dichloromethane and reprecipitated with methanol/acetone (1/1). The copolymers were dried at 80 °C in vacuo. The isolated yields of copolymers **Comp. 235a-c** were 79–85 %

6.3. Synthesis of polythiophenes.

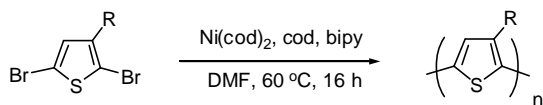
6.3.1. Polymerization of thiophene monomers with FeCl_3 .



[From Ref. 446, © 1991 Elsevier].

Into a 100 mL 3-neck flask equipped with a magnetic stirring bar, condenser, dropping funnel and an inlet for dry air was put 3-alkylthiophene (7 mmol). A solution of anhydrous FeCl_3 (1.0 g) in chloroform (50 mL) was added to the alkylthiophene over about 20 min and the solution became dark. The mixture was then warmed to 50 °C and stirred for 24 h at this temperature, while dry air was bubbled through to remove HCl from the reaction mixture. The black mixture was washed with water to remove excess FeCl_3 to give a dark green-black mixture. This was stirred with conc. aqueous ammonia (20 mL) and chloroform for 30 min at room temperature to produce a yellowish-red chloroform solution of dedoped polymer, which was washed several times with water and dried over MgSO_4 . Removal of the solvent gave 60–97 % yield of the dark purple poly(3-alkylthiophene). Soxhlet extraction with methanol was used to remove the low molecular weight fractions from the bulk polymer.

6.3.2. Yamamoto polymerization.

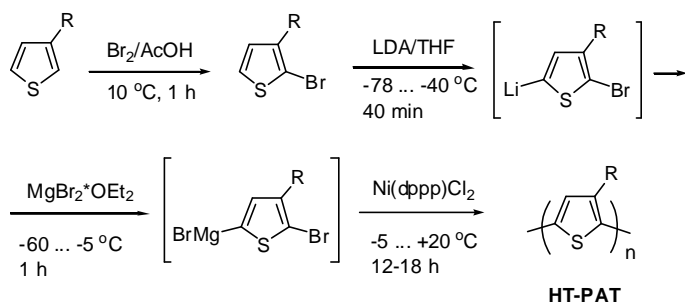


[From Ref. 443 © 1984 Elsevier].

$\text{Ni}(\text{cod})_2$ (1.59 g, 6.00 mmol), 1,5-cyclooctadiene (531 mg, 5.00 mmol), and 2,2'-bipyridyl (937 mg, 6.00 mmol) were dissolved in DMF (20 mL), in a Schlenk tube under argon. To the solution was added 2,5-dibromothiophene (1.21 g, 5.00 mmol) at room temperature. The reaction mixture was stirred at 60 °C for 16 h to yield a reddish brown precipitate. The reaction mixture was then poured into HCl-acidic methanol, and the precipitate of polythiophene was separated by filtration. The precipitate was washed with HCl-acidic methanol, ethanol, hot toluene, a hot aqueous solution of EDTA (pH = 3.80), a hot aqueous solution of EDTA (pH=9), and distilled water in this order and dried under vacuum to yield a reddish brown powder of polythiophene.

When 3-(4-) substituted thiophenes (e.g. 3-hexylthiophene) are used as monomers, the polymers are partly or completely soluble in low polar organic solvents like toluene, chloroform, dichloromethane, tetrahydrofuran. Therefore, after washing with ethanol, the polymer is dried, then dissolved in chloroform and re-precipitated into methanol or acetone to remove low-molecular weight fractions. The solid is collected by filtration, washed with methanol and dried *in vacuo*.

6.3.3. McCullough method of preparation of regioregular HT poly(3-alkylthiophenes).



[From Ref. 451, © 1993 American Chemical Society].

Preparation of monomers: 2-bromo-3-*n*-butylthiophene (**Comp. 378**, R = *n*-C₄H₉).

Into a dry round-bottom flask was placed 68.5 mL (0.8 M) of acetic acid, which was then sparged with argon (5 min). Then 7.7 g (0.055 mol) of freshly distilled 3-*n*-butylthiophene was added. The mixture was cooled to 10 °C, whereupon a 2.5 M solution of bromine (2.8 mL, 0.055 mol) in acetic acid was added dropwise from an addition funnel over a period of 30 min, while the temperature was maintained at 10-15 °C. The material was then stirred in an ice bath for 30 min and was then poured onto ice. The mixture was then extracted into CHCl₃, the CHCl₃ layer washed with NaOH until pH = 6 and dried over MgSO₄ and the solvent removed by rotary evaporation. The product was twice distilled (80 °C / 1.8 mmHg) to yield 5.8 g (48%) of **Comp. 378** (R = *n*-C₄H₉). In similar manner the monomers with R = *n*-C₆H₁₃ (49 %), *n*-C₈H₁₇ (40 %), *n*-C₁₂H₂₅ (41 %) have been obtained.

Polymerization of **Comp. 378** (R = *n*-C₆H₁₃) using 0.5 mol. % catalyst.

Into a dry round-bottom flask was placed dry diisopropylamine (2.11 mL, 15 mmol) and freshly distilled, dry THF (75 mL, 0.2 M). To the mixture was added 6.0 mL of 2.5 M *n*-BuLi (15 mmol) at room temperature. The mixture was cooled to -40 °C and stirred for 40 min. The reaction mixture containing LDA was then cooled to -78 °C, and 2-bromo-3-hexylthiophene (**Comp. 378**, R = *n*-C₆H₁₃) (3.7 g, 15 mmol) was added. The mixture was stirred for 40 min at -40 °C. The mixture was then cooled to -60 °C, MgBr₂·Et₂O (3.87 g, 15 mmol) was added, and the reaction was stirred at -60 °C for 20 min. The reaction was then warmed to -40 °C and stirred for 15 min. The reaction was then allowed to slowly warm to -5 °C, whereupon all of the MgBr₂·Et₂O had reacted. At -5 °C, Ni(dppp)Cl₂ (39 mg, 0.072 mmol, 0.48 mol %) was added. The mixture was allowed to warm to room temperature overnight (≈12–18 h). The polymer was then precipitated with MeOH (300 mL), and the resulting red precipitate was then filtered and washed with MeOH, H₂O, and MeOH again. The solid was then dried under vacuum. Removal of oligomers and impurities was achieved by subjecting the solid to Soxhlet extractions with MeOH first followed by hexanes. The polymer was then dissolved in CHCl₃ using a Soxhlet extractor, the CHCl₃ was removed, and the residue was dried under vacuum to yield 760 mg (36% yield) of 95 % head-to-tail coupled poly-(3-hexylthiophene) **Comp. 378** (R = *n*-C₆H₁₃). The most recent preparation (precipitation with hexane) resulted in 98% HT-HT-coupled polymer. GPC analysis (THF-soluble fraction): *M*_w ≈ 10,000 and PDI = 1.6.

Polymerization of **Comp. 378** (R = *n*-C₈H₁₇) using 2×0.5 mol. % catalyst.

The exact procedure was performed as listed above except on a 18 mmol scale; however, after stirring for 15 h, 0.41 mol % of Ni(dppp)Cl₂ was added (40 mg, 0.074 mmol) at 25 °C. The solution was then stirred an additional 18 h. The polymer was then precipitated with MeOH (400 mL) and allowed to sit for 2 days in MeOH, and the red precipitate was allowed to settle. The solution was decanted and the solid filtered and washed with MeOH, H₂O, and MeOH again. The solid was dried under vacuum and Soxhlet extracted with MeOH and hexanes. The polymer was then dissolved in CHCl₃ using a Soxhlet extractor, the CHCl₃ was removed, and the residue was dried and yielded 2.28 g (65 % yield) of 96%

HT poly(3-octylthiophene). The most recent preparation gave 97 % HT-HT-coupling. GPC analysis (THF-soluble fraction): $M_w = 24,424$ and PDI = 1.98.

6.3.4. Rieke zinc (Zn^*) catalyzed polymerization.

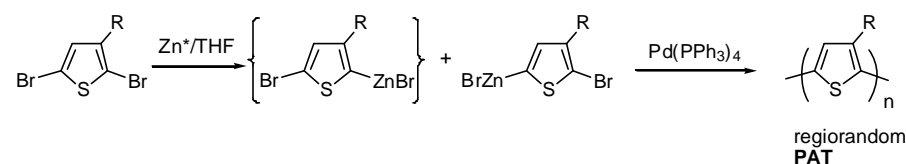
Typical preparation of Rieke zinc (Zn^*)

[From Ref. 458, © 1995 American Chemical Society].

Procedure A. Finely cut (*ca.* $5 \times 5 \times 0.75$ mm) lithium (0.15 g, 22.0 mmol) and a catalytic amount (10 mol %) of naphthalene (0.28 g, 2.20 mmol) were weighed into a 100 mL, two-neck round-bottom flask equipped with an elliptical Teflon stir bar in an argon drybox; the flask was sealed with a septum and a condenser topped with stopcock outlet. Similarly, $ZnCl_2$ (1.50 g, 11.0 mmol) was weighed into a 50 mL, two-neck round-bottom flask, equipped with a stir bar; the flask was sealed with a septum and stopcock. The flasks were then transferred to the manifold system and the argon inlet fitted. THF (15 mL) was added to the flask with lithium and naphthalene while $ZnCl_2$ was dissolved in THF (25 mL). To the flask with lithium and naphthalene, the THF solution of $ZnCl_2$ was transferred via cannula dropwise so as addition was complete in *ca.* 1.5 h under moderate stirring. The reaction mixture was further stirred until the lithium was consumed (*ca.* 30 min), and the resulting black suspension of active zinc thus prepared was ready for use.

Procedure B. Finely cut Li (0.15 g, 22.0 mmol) and a stoichiometrical amount of naphthalene (2.80 g, 22.0 mmol) were weighed into a 100 mL flask, and $ZnCl_2$ (1.5 g, 11.0 mmol) was weighed into a 50 mL flask. The Li and naphthalene were dissolved in THF (20 mL) in *ca.* 2 h. $ZnCl_2$ was dissolved in THF (20 mL) and the solution was transferred into the flask with lithium naphthalide via cannula over 10 min. The reaction mixture was further stirred for 1 h, and the resulting black suspension of active zinc thus prepared was ready for use.

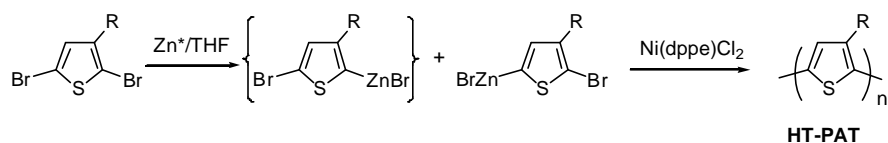
Pd-Catalyzed preparation of regiorandom poly(3-alkylthiophenes) (HT-Comp. 380) from 2,5-dibromoalkylthiophenes (Comp. 381) and Rieke zinc (Zn^*).



[From Ref. 458, © 1995 American Chemical Society].

2,5-Dibromo-3-alkylthiophene (alkyl = $n-C_6H_{13}$ or $n-C_8H_{17}$) (10.0 mmol) in THF (20 mL) was added to the flask with newly prepared Zn^* (11.0 mmol in 40 mL of THF) via cannula at 0 °C, and the mixture was stirred for 1 h at room temperature. A 0.2 mol % amount of $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, in 20 mL of THF) was added via cannula. The mixture was then stirred for 24 h at room temperature (or reflux for 6 h). The polymer was precipitated with a solution of MeOH (100 mL) and 2 N HCl (50 mL), and purified by reprecipitation from the polymer solution of chloroform upon addition of MeOH. After drying under vacuum, red-brown rubber-like polymers of regiorandom PATs were obtained in 97–99 % yields.

Ni-Catalyzed preparation of regioregular HT poly(3-alkylthiophenes) (HT-Comp. 380) from 2,5-dibromoalkylthiophenes (Comp. 381) and Rieke zinc (Zn^*).

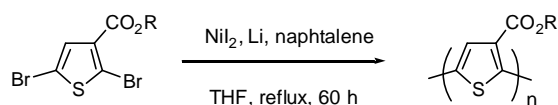


[From Ref. 458, © 1995 American Chemical Society].

2,5-Dibromo-3-alkylthiophene (**Comp. 381**, alkyl = *n*-C₄H₉, *n*-C₆H₁₃, *n*-C₈H₁₇, *n*-C₁₀H₂₁, *n*-C₁₂H₂₅, *n*-C₁₄H₂₉) (10.0 mmol, in 20 mL of THF) was added via a cannula to the newly prepared Zn* (11.0 mmol, in 40 mL of THF) at -78 °C. The mixture was stirred for 1 h at this temperature and allowed to warm to 0 °C naturally in *ca.* 3 h; 0.2 mol % of Ni(dppe)Cl₂ (11.0 mg, 0.02 mmol, in 20 mL of THF) was added via cannula at 0 °C. The mixture was stirred for 24 h at room temperature. A dark-purple precipitate was formed gradually in this period. The mixture was poured into a solution of MeOH (100 mL) and 2 N HCl (50 mL); the resulting dark precipitate was filtered and washed with MeOH and 2 N HCl solution, and then dried. Reprecipitation of polymer from chloroform solution upon addition of MeOH and drying under vacuum gave dark polymer of regioregular HT poly(3-alkylthiophenes). Repurification of polymer by Soxhlet extractions with MeOH for 24 h and then with hexane for 24 h afforded of regioregular **HT-Comp. 380** in 67–82 % yields. The regioregularity of the polymers according to NMR analysis was from 97 to >98.5 % of HT linkage.

6.3.5. Rieke nickel catalyzed polymerization.

Poly(alkyl thiophene-3-carboxylates) (**Comp. 392** and **Comp. 393**).



[From Ref. 476, © 1999 The Ropyal Society of Chemistry].

A 25 mL one-necked flask was charged with NiI₂ (1.563 g, 4.994 mmol), freshly cut lithium (0.080 g, 11 mmol), naphthalene (0.064 g, 0.50 mmol) and THF (10 mL), and the mixture was stirred vigorously at room temperature for 12 h under argon. To the precipitated black nickel powder alkyl 2,5-dibromo-3-carboxylate (R = *n*-C₆H₁₃ or *n*-C₈H₁₇) (2.0 mmol) in THF (5 mL) was added directly via a syringe. The mixture was refluxed for 60 h under argon. The reaction mixture was diluted with diethyl ether to 100 mL, and then filtered to remove the metal powder. The dark red organic phase was washed with water (3 × 50 mL) and dried over MgSO₄. The ether was removed with rotary evaporator, and a dark red solid polymer was obtained. The polymer was extracted with methanol in a Soxhlet extractor for 48 h to remove the low molecular weight material and, after drying under vacuum at room temperature, a red solid was obtained. The yields are 32–33 %.

6.4. Commercial availability of LEP.

To address new researchers entering the field of PLED, especially those, not trained in organic synthesis, we should mention that many LEP are now available commercially from several companies, including Aldrich (www.sigma-aldrich.com), American Dyes Source (www.adsdyes.com), and some others.

In Aldrich, the widest collection belongs to PPV derivatives, which include dialkoxy-PPVs (e.g., MEH-PPV **Comp. 13**, **Comp. 14**), phenyl-substituted PPV **Comp. 43**, meta/para linked PPV copolymer **Comp. 153**, etc. Many monomer precursors for PPV synthesis by Gilch and Wittig procedure as well as the Wessling-Zimmerman precursor **Comp. 2** for unsubstituted PPV are also available.

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